The Cosmic History of the Biogenic Elements and Compounds

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The Cosmic History of the Biogenic Elements and Compounds

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Preface

In inviting me to submit these prefatory remarks, the editors were most generous to recall the speculations (Lederberg, J. and Cowie, D. B., *Moondust,* Science 127:1473-1475 (1958)) that had inspired my own interest in the biological exploration of space 25 yr ago. These started from nothing more tangible than staring at the tables of cosmic abundance of the nuclides, and pondering how condensed matter could have evolved without the production of macromolecules.

Few astronomers then unified their images of condensation with the valence theory of chemistry. The overabundance of hydrogen is indeed an embarrassment to remind us that the prevalence of any organic molecules less reduced than methane is out of equilibrium: that fact given, we should be little more surprised to find complex organic molecules in interstellar space than on Jupiter or in the comets. From that perspective, Earth's advantage is in having most of its hydrogen blown away, though not to the extremes that Mars seems to show. That is, an Earth more reduced than our planet would have difficulty in sustaining organic molecules beyond methane: a model inverted from some other conventional representations. If we accept the stability of such molecules on a reduced Earth, why not also in space? Why look later than the primary condensation for the abundance of carbonaceous species that we must postulate as a precondition for the emergence of life? Indeed, any process that permits the large-scale production of oligomeric carbon could hardly avoid its polymerization, opening further questions as to the selective factors that would condition the chemical forms of large-scale condensed matter. Planetary bodies would furnish idiosyncratic local environments; but most of that matter would be found in the relatively homogeneous interstellar space. We could then ask for a unifying cosmic description of the primary modality of chemical evolution. To the biologist, this perspective does not yet advance our understanding of the origin of life – the really difficult enigma remaining still being the progression from random to well-ordered and self-replicating polymers. A cosmic seat of early biological evolution does alter the locus of improbabilities, from the anthropic curiosity that life could start on one planet, to an improbable universe which nevertheless generated life. With what a priori probability we cannot say: does the cosmic condensation already furnish enormous quantities of matter preadapted to the requirements of biological macromolecules? Will we find the raw material of DNA already present there?

These were naive and elementary questions, hardly to be justified even as assertions. Nevertheless, they have been greatly bolstered by the experimental and observational work of the last two decades, as evidenced by the report of this study group.

Perhaps the most foolish bit of wishful thinking expressed in 1958 was the expectation that the surface of the Moon, presumably unweathered, would show some accumulation of primitive condensate. At that time, regolith models with extensive reworking of planetary surfaces by tectonic and meteoritic activity were less widely understood. For the same reason today, we should perhaps be cautious in our expectations of cometary composition; nevertheless,

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this doubtless provides the closest approximation to accessible samples of "interstellar matter" we are likely to achieve for some time.

As to Mars, the possibility of life (and certainly of fossil life) should not be written off as quickly as some authors might admit. We have as yet sampled only two (very similar) habitats; there remain many enigmas of fossil drainage patterns, as well as the unexplored polar cap zones.

Altogether, we are at a stage at which each new finding raises many more new questions than it puts to rest; and many of the most trenchant questions are well stated in the study. The greatest value of the intellectual synthesis given in this volume is its provocation of new experiments and measurements focused on very large and important aims – important for theoretical understanding of our own origins, and with grave practical import ranging from earthquakes to energy sources on our own planet.

Joshua Lederberg
The Rockefeller University

1

Introduction

The roots of humanity's interest in the origins of life extend deep into antiquity: Our earliest conceptions of the process were expressed in the creation myths of emerging cultures. It was not until the twentieth century that the origins of life became widely recognized as a subject amenable to scientific study. According to modern theory, living organisms arose naturally on the primitive Earth through a lengthy process of "chemical evolution" of organic matter that began with the synthesis of simple organic compounds from inorganic precursors in the atmosphere; continued in the oceans, where these compounds were transformed into increasingly complex organic substances; and culminated with the emergence of organic microstructures having the capabilities of rudimentary self-replication and other biochemical functions.

Historically, the Life Sciences Division of NASA Headquarters has played a central role in the establishment of a scientific program to study the origin of life on Earth and elsewhere in the universe. Over the past 20 yr, this study has been conducted in three areas corresponding to the major elements of NASA's Exobiology Program: chemical evolution, the origin and early evolution of life, and the search for life and life-related compounds in the solar system.

Acting on the mandate of its charter, NASA has carried humanity's quest for new frontiers into space, seeking along the way answers to questions of fundamental importance to the life sciences: Is there life on other planets? How did life originate on Earth? What was it about Earth's origin and development that made possible the origin of life? This search has followed the path of planetary exploration to the Moon, Mars, Venus, and the giant planets and their satellites. As a result of knowledge gained from these explorations and from the study of Earth itself, it has become clear that planetary evolution and chemical evolution are inextricably intertwined. Progress along the path toward the origin of life may be terminated at any stage, however, if the physical or chemical history of a host planet takes the wrong turn.

At the time when NASA began launching its spacecraft toward other planets, discoveries of a less spectacular nature, but of fundamental importance to a general theory of the origin of life, were being made in the fields of astrophysics and cosmochemistry. Organic compounds in increasing numbers and complexity were being detected in the interstellar medium; and a variety of organic compounds of the sort composing living systems, but of unequivocally extraterrestrial origin, were identified in the Murchison carbonaceous chondrite. These findings demonstrated clearly that the chemical evolution of organic matter was not restricted to planets, but occurred widely in the universe as an integral part of cosmic evolution.

Throughout history, humanity's creation myths appear to reflect each culture's perceptions of the dimensions of its universe and its place within it. Today, the scope of those perceptions has expanded beyond the reaches of the solar system to the stars and interstellar clouds that populate the seemingly limitless expanse of space. Just as biological evolution implies that all organisms arose by divergence from a common ancestry, so cosmic evolution implies that all matter in the solar system had

a common origin. And life may be viewed as the product of countless changes in the form of primordial stellar matter wrought by the processes of astrophysical, cosmochemical, geological, and biological evolution.

In the larger context of cosmic evolution, the chain of events that led to the origins of life extends beyond planetary history to the origin of the solar system, to processes operating in the interstellar clouds that spawn stars like the Sun, to the very birth in stars of the elements that make up living organisms, the biogenic elements. Indeed, the links in this part of the chain constitute *the cosmic history of the biogenic elements and compounds*, a history that holds the promise of life widespread in the universe. When viewed from this perspective, NASA's Exobiology Program seems to be somewhat narrow in scope; augmentation of its existing components with a modest new research effort that encompasses this cosmic history would appear to be timely and appropriate.

The objectives of this report are to (1) address the scientific issues pertinent to the cosmic history of the biogenic elements and compounds, and (2) identify the opportunities that exist for fruitful research across many disciplines using theoretical, experimental, and observational approaches. This report is intended to serve as a scientific guide both for investigators interested in conducting research in the cosmic history context and for the Life Sciences Division of NASA Headquarters in its development of this new program component.

The biogenic elements are those generally judged to be essential for all living systems. For the present purposes primary emphasis is placed on the elements hydrogen (H), carbon (C), nitrogen (N), oxygen (O), sulfur (S), and phosphorus (P). The compounds of major interest are those normally associated with water and with organic chemistry, in which carbon is bonded to itself or to other biogenic elements. The essential elements usually associated with inorganic rather than organic chemistry are also included—e.g., iron, magnesium, calcium, sodium, potassium, and chlorine—but they are given secondary emphasis.

Three kinds of scientific issues are considered. The first and most important attempts to trace the physical and chemical pathways taken by the biogenic elements and compounds from their origins in stars to their incorporation in the preplanetary bodies by which they were distributed throughout the solar system. The second deals with the kinds of measurements that can be made on the biogenic elements and compounds in the galaxy and solar system in order to develop theories about the formation of the solar system and the chemical evolution of life. In many respects these first two issues are two sides of the same coin. The third considers the ways in which the physical and chemical properties of the biogenic elements and compounds may have influenced the course of events during the formation of the solar system and the bodies in it.

The chapters in this report are organized in a sequence that follows a logical development of the cosmic history. The next chapter provides an overview of the major epochs in this cosmic history, starting with nucleosynthesis and ejection of the biogenic elements from stars, proceeding through interstellar clouds, cloud fragmentation and protostellar collapse, evolution of the solar nebula, accretion of solid objects in the nebula, and ending with chemical evolution in planetoids. Chapters III-VIII treat each of these epochs in detail. Each chapter provides a general assessment of our current knowledge, and each identifies areas in which fruitful research can be conducted. Chapter IX summarizes specific research areas in which major gains in our understanding of the evolution of the biogenic elements and compounds can probably be made in the next 5-10 yr.

RECOMMENDATIONS

In the course of its activities, the Study Group that prepared this report reached the following conclusions regarding the cosmic history of the biogenic elements and compounds as a field of research:

1. It is consistent with NASA's mission in space and offers opportunities to address many questions of high scientific merit, using both ground-based facilities and spacecraft.

2. It embraces major scientific issues that are relevant to an understanding of the origins and distribution of life in the universe.

3. It is a timely and important extension of the NASA Life Science Division's Exobiology Program.

The Study Group makes the following recommendations:

1. That the Life Sciences Division of NASA initiate a modest new study of the cosmic history of the biogenic elements and compounds. This study should be developed within the context of the Exobiology Program.

2. That NASA apply its expertise in astrophysics, astronomy, and cosmochemistry to the scientific problems that are identified. This expertise should include technological developments in the instrumentation of ground-based facilities, and Earth-orbiting and planetary spacecraft.

3. That NASA include the scientific objectives embodied in the study of the cosmic history of the biogenic elements and compounds wherever appropriate in the development of its missions for the exploration of the solar system and space.

ACKNOWLEDGMENTS

This report was prepared under the auspices of the Life Sciences Division of NASA Headquarters. The scientists who wrote it were assembled into a Study Group under the chairmanship of Dr. John A. Wood, of the Harvard-Smithsonian Center for Astrophysics. Two "Science Workshops on the Cosmic History of the Biogenic Elements and Compounds" were convened by the Study Group, in January 1982 and May 1982. These 3-day meetings were held, respectively, at the NASA Ames Research Center, and at the Center for Astrophysics in Cambridge, Massachusetts. The Study Group was aided in its efforts by the following scientists who presented tutorials at the workshop and assisted the authors of the report in their writing: Sheldon Aronowitz, Gustav Arrhenius, A. G. W. Cameron, Patrick M. Cassen, Douglas J. DeFrees, Bertram Donn, Bruce T. Draine, J. Mayo Greenberg, Richard Greenberg, Typhoon Lee, Robert O. Pepin, George W. Wetherill, and Steven P. Willner. Their assistance is gratefully acknowledged.

The Study Group members consider this to be one jointly authored publication. However, their contributions to particular chapters were concentrated as follows: Chapter I, Chang; Chapter II, Wood; Chapter III, Wannier and Werner; Chapter IV, Herbst; Chapter V, Black and Scoville; Chapter VI, Chang, Delsemme, Herbst, Kerridge, Prinn, and Wood; Chapter VII, Black; Chapter VIII, Bunch, Chang, Delsemme, Hayes, and Kerridge; Chapter IX, all.

We are grateful to John Billingham, Chief of the Extraterrestrial Research Division at NASA Ames Research Center, and Donald DeVincenzi, Chief of Research and Technology Development in the Life Sciences Division at NASA Headquarters, for their support and encouragement in the preparation of this report. The hospitality of George B. Field, Director, and the Staff of the Harvard-Smithsonian Center for Astrophysics is greatly appreciated.

Special thanks are due to Karen Motylewski for organizational work, and to Mary Jeffers for secretarial support.

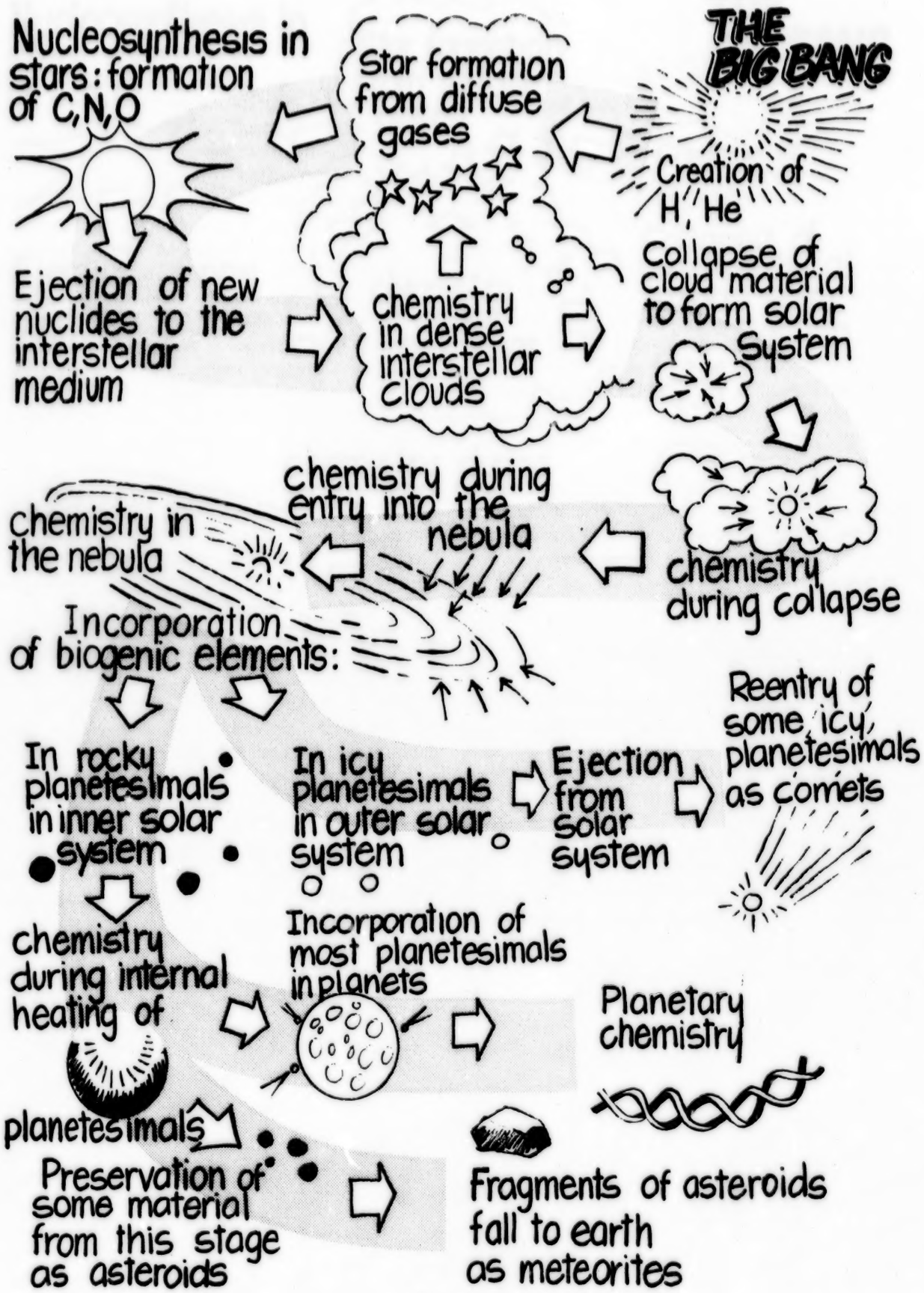
Nucleosynthesis in stars: formation of C, N, O
Star formation from diffuse gases
THE BIG BANG
Creation of H, He
Ejection of new nuclides to the interstellar medium
chemistry in dense interstellar clouds
Collapse of cloud material to form solar System
chemistry during entry into the nebula
chemistry in the nebula
chemistry during collapse
Incorporation of biogenic elements:
Reentry of some icy planetesimals as comets
In rocky planetesimals in inner solar system
In icy planetesimals in outer solar system
Ejection from solar system
chemistry during internal heating of
Incorporation of most planetesimals in planets
Planetary chemistry
planetesimals
Preservation of some material from this stage as asteroids
Fragments of asteroids fall to earth as meteorites

Figure 1.

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II

An Overview of the Cosmic History of the Biogenic Elements

Discussions of prebiotic chemistry generally treat processes on primitive planets or in the solar nebula. However, it is abundantly clear from astrophysics that the carbon atoms of the solar system had a long and complex chemical history before the Sun was even formed; so that by the time it was incorporated in planets or the nebula, much of the solar system's carbon already may have been in the form of complex organic molecules. The present document reviews our current understanding of the pre-planetary history of carbon and the other elements most important to life processes. A flow-chart of ancient events and processes is shown in figure 1.

The ultimate beginning of things, the Big Bang, created an expanding universe of hydrogen and helium atoms, but no carbon (chapter III). The first generation of stars formed out of these light elements. (More information follows about the process of star formation.) A newly formed star goes through a process of contraction, during which potential energy is converted to heat; part of the heat is radiated away, and the rest increases the internal temperature of the star.

By the time an interior temperature of $\sim 10^7$ K is reached, atoms in the stellar core are colliding with one another so energetically that nuclear fusion reactions occur, releasing nuclear energy as heat. When a star's rate of nuclear heat generation becomes large enough to balance its radiative heat loss, it stops contracting and enters a long, stable phase of stellar evolution, while its internal store of hydrogen is being slowly consumed. Stars on the main sequence of the Hertzsprung-Russell diagram of astrophysics are in this "hydrogen-burning" stage of evolution.

The product of hydrogen-burning is helium. When the core hydrogen of a first-generation star becomes depleted, further shrinkage of its interior occurs, temperatures increase, and at $\sim 10^8$ K a new series of nuclear fusion reactions is initiated in which the helium "ashes" from hydrogen-burning "burn" to form heavier nuclides, in particular carbon-12 and isotopes of oxygen. The cosmic history of the biogenic elements might be said to start at this point.

It is important to understand that stars are not eternal, immutable bodies, as the poets would have it. They are born, they mature, and they die. The lifetimes of most stars are less (in many cases very much less) than the present age of the universe. The death of a star often involves an extremely violent event—a supernova—that casts much of its internal substance out into the space between stars (the *interstellar medium*). Even larger amounts of processed stellar matter are lost from stars while they are in the prime of their lives through stellar winds, fluxes of energetic ions that continually diffuse away from all stars (e.g., the solar wind). Thus the helium, carbon, and oxygen created in the first-generation stars are not forever entombed in them, but are returned to a pool of elements in the interstellar medium, where they are available for future use.

Second- and later-generation stars that form from the interstellar medium incorporate carbon and oxygen atoms from the very beginning, and the presence of these heavier nuclides in their cores promotes more complex patterns of nuclear reaction than simple hydrogen-burning.

These reactions produce the full range of stable isotopes of carbon, nitrogen, and oxygen, some fraction of which is ultimately fed back to the interstellar medium.

Thus the elemental and isotopic composition of the interstellar medium is constantly evolving. When the solar system formed from the interstellar medium $\sim 4.6 \times 10^9$ yr ago the galaxy was already $\sim 10^{10}$ yr old, and the composition of its interstellar medium was highly evolved. The set of nuclides we inherited have a complex genealogy which interweaves through numberless stars now dead and gone, where the individual atoms resided for a time and, in many cases, were transmuted into new nuclides.

This much has made it sound as though the interstellar medium is a homogeneous reservoir of individual atoms, waiting to be incorporated in new stars. Actually the interstellar medium is highly structured, and it contains dust and molecules, the products of chemical processes of great complexity (chapter IV), as well as atoms and ions. Much of the dust and some of the molecules were produced in the envelopes of red giant stars, from cooling gases immediately after they were expelled from the stars in stellar winds.

There are distinctly different regimes of mass and energy density in the interstellar medium, ranging from molecular clouds (10^3-10^4 molecules/cm^3, 5-10 K) to the intercloud medium (0.1-1 atom/cm^3, ~5000 K). Roughly 10% of the mass of our galaxy is in the interstellar medium; the rest is in stars. Most of the interstellar material, ~80% of it, resides in clouds. Only ~20% × ~10% = ~2% of the galaxy's mass is dispersed in the intercloud medium, which occupies ~50% of the volume of the galaxy.

The intercloud medium is a very hostile environment for molecules. They are promptly photodissociated by ultraviolet (UV) radiation, leaving only atoms and ions as constituents of the intercloud gas. Interstellar clouds are relatively opaque to UV radiation, however, and in them molecules not only can survive but can react to form new and more complex molecules. Radio astronomy has detected molecules as complex as HCCCCCCCCCN in interstellar clouds. Several classes of molecular reactions can occur: gas phase reactions, usually involving reactants that have been ionized by cosmic rays or UV radiation; reactions between species adsorbed on the surfaces of dust grains; and possibly reactions in icy layers or mantles that condense onto dust grains in the very cold molecular clouds. The latter mechanism depends on a local UV flux sufficiently intense to photodissociate molecules in the ices, forming free radicals. Laboratory experiments have shown that when such a system of frozen radicals is warmed up, reactions between the radicals produce molecules of great complexity, including involatile material resembling terrestrial kerogens.

Interstellar clouds are also where stars are formed, so the raw material a star is given to start with includes biogenic elements in a state of some molecular complexity, as suggested above, not merely atoms of carbon or molecules of CO and CH_4. The substance of interstellar clouds is pulled together by mutual gravitational attraction, but held apart by gas pressure, turbulent motions, and magnetic fields. Under circumstances that are rather poorly understood, the gravitational side of the struggle sometimes prevails locally, and a portion of an interstellar cloud begins to collapse upon itself (chapter V). Initially many times more massive than a star, the cloud fragments into smaller units as it collapses. Some of these will ultimately become stars.

The gravitational collapse of a cloud fragment into a star proceeds nonuniformly. At first, material from near the center of the precursor cloud fragment comes together into a small protostar: in the case of our Sun, the protosun was at first perhaps comparable to the present planet Jupiter in mass. For a period of roughly a million years after the protostar forms, additional gas and dust from the outer zones of the cloud fragment continues to fall into the stellar system and become part of it.

As the cloud center collapses, compression of its gases generates heat. During the early stage of collapse the gas is transparent enough to allow this heat to be radiated away, and the gas stays cold. After compression increases the gas density beyond $\sim 10^{10}$ molecules/cm^3, however, the cloud material becomes increasingly opaque to radiation (mostly because of the dust grains embedded in it), and compressionally generated heat is trapped in it. Temperatures (and pressures) mount as the system

continues to collapse, until a pressure is attained that is large enough to counterbalance the gravitational force that is pulling the system together. At this point collapse of the cloud center ceases, and its material forms a quasi-stable structure: the protostar spoken of above. The protostar is not yet hot enough inside to promote nuclear fusion, but with continued radiation, contraction, and the gain of additional in-falling cloud material, it will become so in about a million years.

Not all of the late-arriving cloud material falls onto the protostar. This is because the material of the interstellar medium has a certain amount of angular momentum, a fraction of which is conserved as the system collapses. Because of its angular momentum content, an element of cloud material in free-fall generally does not drop directly onto the protostar, but instead attempts to describe a near-parabolic orbit around it. Near the protostar, however, it collides with cloud material arriving from other directions. The motions of many such elements of material feeding into the protostellar system are averaged out into that of an *accretion disk* of gas and dust, rotating at Keplerian velocities about the protostar, in a plane perpendicular to the net angular momentum vector of the star's precursor cloud fragment.

Rotational velocities vary with radial distance in the accretion disk, so there is shearing motion between annular elements in the disk. The shear is resisted by viscosity of the disk gases, which has the effect of redistributing mass, energy, and angular momentum in the disk; it also heats the disk gases to some extent. As a result of these redistributions, much of the substance of the disk is ultimately fed into the protostar, increasing its mass.

Our planetary system is understood to have formed in the accretion disk associated with the protosun: the term commonly applied to this disk is the *solar nebula* (chapter VI).

Much uncertainty attaches to the amount and disposition of angular momentum inherited by the solar system. This unknown quantity crucially affects the planet-forming process in the nebula. If the solar system's precursor material had relatively little angular momentum, most of the material would have joined the protosun immediately, the nebula/protosun mass ratio would have remained small, the nebula would have been a gravitationally stable structure, and planet formation would have proceeded via the accretion of solid grains in the nebula into larger and larger bodies. If the precursor material had large specific angular momentum ($\gtrsim 10^{19}$ cm^2/sec), however, most in-falling material would at first join the nebula rather than the protosun, a large nebula/protosun mass ratio would have caused the nebula to be gravitationally unstable, and the latter would have fragmented into an assemblage of gaseous protoplanets, each in orbit about the center of mass of the system. In this case, many of the crucial steps of planet formation would have occurred inside the protoplanets.

This document concentrates its discussion on the former possibility (the gravitationally stable nebula), partly because most of the workers in the planetary sciences community favor it and publish discussions in this context, and also because consequences of the protoplanet option are more model-dependent and less testable than are events and processes in an integral nebula. Note that neither of these is a really sufficient reason for discounting the gaseous protoplanet model.

In-falling interstellar gas encountered a standing shock front at the surface of the nebula, where it was compressed and heated. (The heat was soon lost by radiation as the gas passed behind the shock front.) Dust grains falling toward the nebula were irradiated by UV radiation from the protosun, and warmed by it. It is possible that the icy mantles-to-kerogens reaction sequence described earlier occurred at this stage of in-fall, so that interstellar grains arriving at the solar nebula were coated with sticky, refractory, organic compounds. After dust grains crossed the shock front, they were decelerated and to some extent heated by drag in the nebular gases. At some times and places in the shock front, shock and drag heating would have been severe enough to dissociate gaseous organic molecules and pyrolyze condensed compounds, reducing the previous complexity of presolar biogenic molecules to the simplicity of individual atoms and small molecules. At other times and places this would not have been the case, and complex presolar molecules were introduced more or less intact into the nebula.

In the nebula a variety of types of chemical reactions were at work, remaking the molecular chemistry of the biogenic elements. In the hotter zones of the nebula, straightforward equilibrium gas-phase reactions would have established the biogenic elements in molecules of CO, N_2, and H_2. Elsewhere, nonequilibrium processes were probably important. One possibility is Fischer-Tropsch-type reactions, whereby the catalytic effect of certain mineral grain surfaces is to create complex, nonequilibrium, organic molecules. Laboratory simulations have produced amino acids, among other compounds, by this means. Other mechanisms are reaction sequences based on photochemistry and high-energy particle irradiation. Possible sources of the required UV radiation and particles are the protosun, neighboring stars, and lightning discharges promoted by charge separation in the turbulent gases of the nebula.

Ultimately, some fraction of the biogenic compounds in the nebula, whether produced in the nebula or accepted unchanged from the interstellar medium, was stabilized in condensed matter that became planets, satellites, asteroids, and comets. The biogenic compounds may have condensed (especially in the outer solar system), or they may have been adsorbed on or trapped within inorganic mineral grains. A sticky organic coating on tiny mineral grains might have been instrumental in causing them to accumulate into larger aggregations, of roughly centimeter dimension, which were more responsive to gravitational forces than to the buffeting of the thin, turbulent nebular gases.

Aggregations this large would have tended to settle to the midplane of the nebula, and accumulate there in a thin layer of relatively high local mass density. Such a layer of solids can be gravitationally unstable, even if the embedding gaseous nebula is not. Instability is thought to have caused a layer of this type in the solar nebula to fragment into discrete concentrations of dust clumps, each of which drew together into a mass of roughly kilometer dimensions (chapter VII); we refer to these as *planetesimals*.

Eventually the solar nebula was dispersed. The details of this important event are very poorly known. Much of the substance of the nebula was absorbed by the Sun. Some is likely to have been driven away by a highly enhanced solar wind during a particular stage of premain-sequence solar evolution (the T Tauri stage), and some may have been expelled by the nebula's own "wind," an outflow analogous to the solar wind. Dust still unaggregated would have been carried away with the nebular gases, wherever they went. A large number of small bodies in the early stages of accretion, planetesimals and planetoids (see below), were left orbiting the protosun.

In the outer solar system, where nebular temperatures were always very low (<150 K) and the compounds of biogenic elements were condensible, the planetesimals consisted largely of ices of these elements. The ices predominated over dust grains because the solar system abundances of carbon, nitrogen, and oxygen are 10-20 times greater than the abundances of silicon and the other inorganic-mineral-forming elements. Most of these icy "snowball" planetesimals were eventually swept up by the outer planets as they grew. Some, however, on passing close by a massive outer planet, were thrown into eccentric orbits with aphelia far out in interstellar space.

The gravitational influence of neighboring stars further modified a few of these eccentric orbits, lifting their perihelia out of the planetary system. Many icy planetesimals have remained to the present day in these highly modified orbits, coasting slowly in huge elliptical orbits tens of thousands of astronomical units away from the Sun.

Sometimes these objects are gravitationally affected yet again by a neighboring star, and occasionally one has its perihelion dropped back into the inner solar system. When such a snowball follows its ordained track and approaches the Sun, its ices begin to vaporize and stream away from it, and we have a new comet. Comets are the repositories of the most primitive, best preserved, but most fragile nebular and presolar materials still surviving. We study them from afar with intense interest, and yearn for the opportunity to send spacecraft missions to them.

In the inner solar system, planetesimals accumulated into a generation of larger objects (~100-km diam) which this document calls *planetoids* (chapter VIII). Planetoids have survived as such in the zone between Mars and Jupiter; today we call them asteroids. At smaller

radial distances, the planetoids were all swept up by the growing terrestrial planets, or else were ejected from the solar system by close planetary encounters.

Meteorites are fragments of asteroids, therefore samples of planetoids. The substance of many meteorites has been little changed since the time of the planetoid's accretion, so we study them carefully to learn about chemical and physical processes in the nebula, and also about pre-solar events.

The planetoids were not such faithful preservers of ancient biogenic compounds as were the comet nuclei, however, which accumulated in the "deep-freeze" of the outer solar system. It is clear from the properties of the meteorites that many of the planetoids experienced a brief, fierce, heating event soon after they accumulated. The cause of this is not known, but a strong possibility is that they contained a short-lived radioactive nuclide, ^{26}Al, in concentrations adequate to cause the observed thermal effects.

Some planetoids were actually melted. Others were not melted, but were metamorphosed at temperatures up to ~1300 K for millions of years. As we would expect, biogenic compounds are not found in the meteorite classes derived from these planetoids. Other meteorites have been only mildly metamorphosed, and in them we find a rich array of organic compounds. These meteorites, the carbonaceous chondrites, have been studied intensively for the information they contain about the chemistry of the biogenic elements in the solar nebula, in newly accreted planetoids, and possibly in the pre-solar interstellar medium.

This is as far as we carried the history of the biogenic elements and compounds. Their further evolution in full-scale planets is the topic of other study groups and researchers. We feel that the first chapters of the story are as interesting as the rest of the book, however, and we believe future research in this area will be very rewarding.

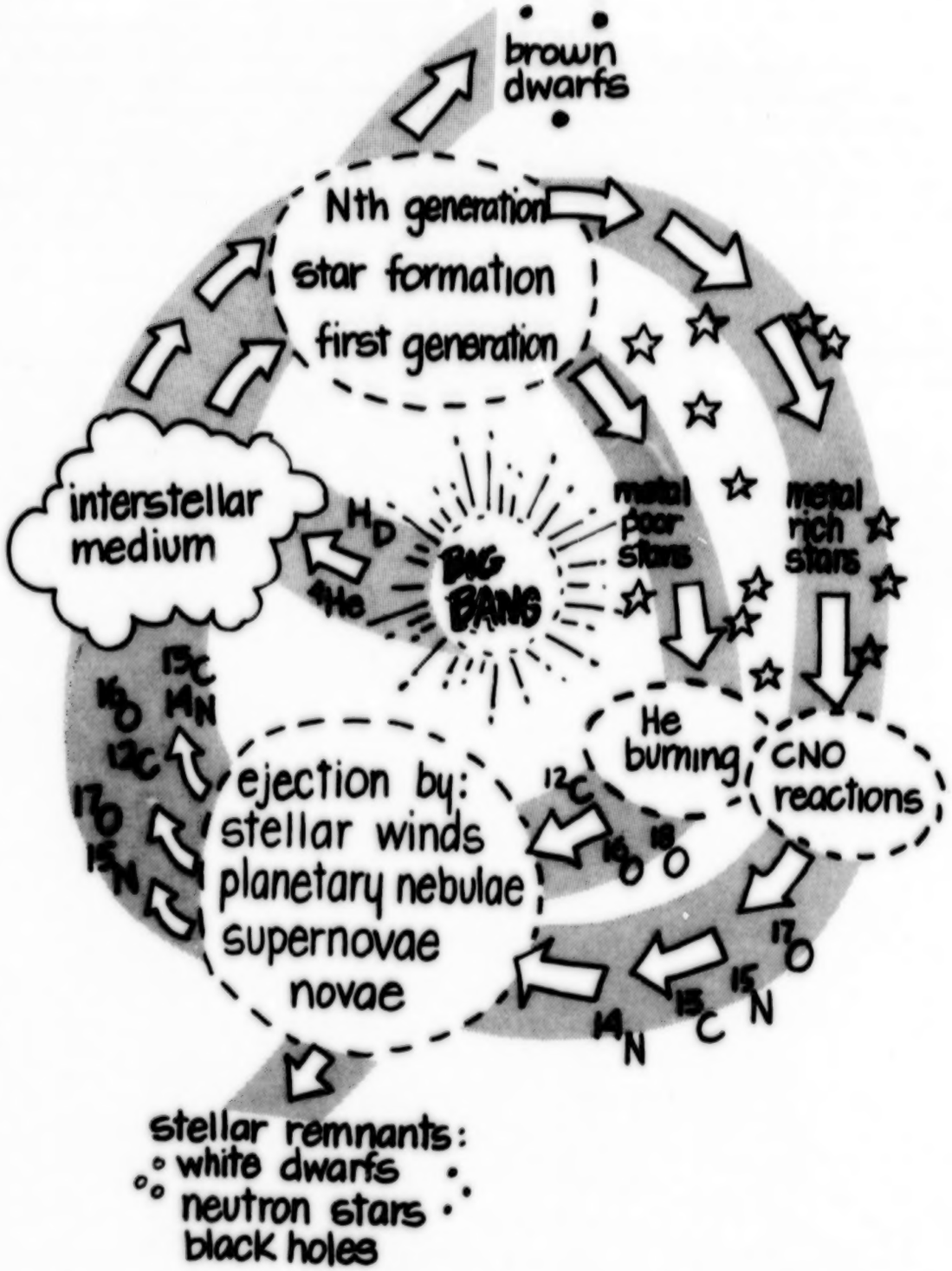
brown dwarfs
Nth generation
star formation
first generation
interstellar medium
H
D
4He
BIG BANG
metal poor stars
metal rich stars
He burning
CNO reactions
ejection by:
stellar winds
planetary nebulae
supernovae
novae
13C
14N
16O
12C
17O
15N
18O
stellar remnants:
white dwarfs
neutron stars
black holes

Figure 2.

III

Nucleosynthesis and Ejection to the Interstellar Medium of the Biogenic Elements

Practically all the chemical elements play some role in life processes, but in this review we define as the "biogenic elements" carbon, nitrogen, oxygen, and hydrogen, and to some extent sulfur and phosphorus. The creation of the biogenic elements is a continuing process in which cosmic material is cycled through a number of stages of nucleosynthesis. Because some of these stages must occur in successive generations of stars, the cosmic elemental abundance pattern was shaped during repeated episodes of star formation and stellar mass-loss and involved physical processes in the interstellar medium (ISM) as well as in the dense cores of stars where most nucleosynthesis actually occurs. The astrophysical processes involved, which are to some degree cyclic, are shown in figure 2.

The first element-forming event was, of course, the Big Bang. The primordial material formed in the Big Bang consisted almost exclusively of the isotopes of hydrogen and helium. The processing of primordial material into heavier elements began with its incorporation into stars, the first of which were necessarily metal-poor. (The terms "metal-poor" and "metal-rich" will be used in the usual astronomical sense, in which all elements heavier than H and He are "metals.")

In stars of sufficient mass, fusion reactions occur which build up the abundances of heavy elements. Depending upon the details of stellar evolution, these reaction products may be redistributed within the star and may be expelled back into the ISM by one of several means. The processed and expelled material, enriched to varying degrees in isotopes of the heavy elements, is then available for incorporation in later generations of metal-rich stars, where additional nuclear processing occurs. On the other hand, during the formation and death of stars dense stellar remnants can be formed which are inert, in the sense that material within them is forever removed from the cycle of nuclear processing and mass ejection. The composition of these remnants is not relevant to the present discussion.

THE EVOLUTION OF NUCLEAR ABUNDANCES

The general concept of nucleosynthesis expressed in figure 2 is supported by a variety of theoretical arguments and observational facts. Stars are seen to be composed largely of hydrogen, and to have energy requirements that can be met only by hydrogen fusion reactions. Stellar modeling studies have shown that heavy elements can be synthesized in or around cores exhausted of hydrogen fuel. Theoretical studies of possible nucleosynthesis during the Big Bang show that this initial event could not have produced the nuclides heavier than helium, especially in their observed pattern of relative abundances. On the other hand, the current abundances of the heavy elements are consistent with their cumulative production by stars in our galaxy.

In addition to these general arguments, the history of stellar heavy-element enrichment can be read directly from a variety of more detailed observations. A commonly employed method of tracking the evolution of elemental abundances is to look for a relationship between the estimated ages of stars and the compositions of

their atmospheres. It is assumed that when a star condenses it incorporates material whose composition is representative of the ISM at that time; and thereafter the composition of the star's atmosphere does not change further, but continues to record the ISM composition at the time the star formed. Examples of older objects studied for this purpose are globular clusters and certain high-velocity or low-mass stars. Young objects include massive stars, stars in the galactic disk, and, youngest of all, interstellar clouds. Studies associating age with composition are carried out most easily in our galaxy. In all cases, there is observational support for an increase in the abundances of the heavy elements with time.

The total extent of heavy-element buildup in a particular region of space would be a function not only of the age of the material in question, but also the rate at which it has been processed through stars. Additional evidence for progressive nucleosynthesis comes from an observed association of low metallicity with regions in a galaxy where the past rate of stellar processing has been small. Such regions typically have low average material density, are found at large galactic radii, and have relatively large gas/star mass ratios. Denser regions at smaller galactocentric radii are expected to show greater enrichments. Spatial variations of composition along these lines can be observed in external galaxies as well as in our own.

As an indicator of nuclear processing, metallicity is only one of several measurable quantities. Among the biogenic elements, each stable isotope has its own distinctive nuclear history and specific sites for possible production. The available evidence for abundance gradients comes primarily from observations of elemental abundances (from UV, optical, and infrared (IR) spectroscopy) and from millimeter-wave observations of relative isotope abundances.

Elemental Abundances

Optical and UV observations of HII regions (i.e., where hydrogen is ionized) and planetary nebulae give information about relative elemental abundances; notably those of oxygen, nitrogen, carbon, and sulfur relative to hydrogen. On the whole, observational results indicate the presence of significant radial gradients of the elemental ratios O/H, N/H, and C/H, in the sense that these ratios decrease with increasing distance from the galactic center. Galactic HII regions are valuable for studies of radial gradients because they lie in the galactic disk, where elemental abundances are evolving rapidly, yet they are sufficiently massive that their compositions are not significantly perturbed by the contributions of individual stars. On the other hand, such studies are rendered difficult by the limited number of visible HII regions, and by the large range of their physical parameters such as density, temperature, size, and the spectrum of ionizing radiation.

The results of HII region studies in our own galaxy indicate local abundance variations which, when extrapolated to the galactic center, at a distance of 10 kpc (kpc = kiloparsecs. One parsec (pc) = $\approx$3.26 light years (ℓy) = $\approx 3 \times 10^{18}$ cm), imply variations of C/H, O/H, and N/H by about a factor of 10. Because of problems caused by high optical extinction in the galactic disk, these results should be used in conjunction with studies of external galaxies. Unless an external disk galaxy happens to be viewed edge-on, optical extinction is not a serious problem. The presence of O/H, N/H, and N/S gradients in open spiral galaxies seems well established. These abundance gradients, especially in the galaxy M101, are in close agreement with those derived for our galaxy. Another galactic abundance gradient which has received attention is that of N/O. Although the state of current observations is somewhat controversial, there is some evidence for significant N/O radial gradients in several external galaxies, consistent with more rapid stellar processing at smaller galactic radii.

Elemental abundance gradients can also be observed among planetary nebulae. Again, there is some evidence for gradients in the ratios of N/H and O/H among planetary nebulae in our galaxy, but care must be taken in such studies to distinguish between the abundances at the time of stellar formation and possible changes in abundances brought about by nucleosynthesis in the parent star.

Isotopic Ratios

Isotopic abundances in our galaxy can be measured by means of the isotopic shifts in millimeter-wave and IR transitions of molecules.

Isotopic abundance determinations have the advantage that they sidestep some difficult interpretational problems which may be present in elemental abundance determinations due to the very different physical and chemical properties of the elements. Also, millimeter-wave lines in dense clouds can be observed throughout the galactic disk, in contrast to the limited range of optical and UV observations. Thus far, results in our galaxy indicate a distinct evolution in the CNO material in the galactic center region, but constant isotopic abundances throughout the rest of the galactic disk. These results contrast with those obtained from elemental abundance studies (above), and indicate a general uniformity of nuclear processing in the galactic disk. The available millimeter wave observations have measured $^{18}O/^{17}O$, $^{12}C/^{13}C$, $^{32}S/^{34}S$, $^{16}O/^{18}O$, and $^{14}N/^{15}N$, and all are incompatible with variations in these ratios by as much as a factor of two between 5.5 and 12.5 kpc from the galactic center.

NUCLEOSYNTHESIS IN STARS

Aside from hydrogen, the most important of the biogenic elements are carbon, nitrogen, and oxygen. The isotopes of these elements are shown in table 1, along with the most important mechanisms of production and expulsion. Most of the basic nuclear processes are represented among the production mechanisms of these nuclides. These mechanisms are of two types, namely those that proceed hydrostatically and those that proceed explosively. The latter occur in such sites as the Big Bang, supernovae, novae, and possibly a speculative early population of supermassive objects. The elements heavier than oxygen, which are expelled almost exclusively by supernovae, are discussed separately. The spallation of interstellar material by cosmic rays plays a relatively minor role in the nucleosynthesis of these elements.

Deuterium and the Big Bang

The implications of the abundance of deuterium to cosmology are well known. It is thought that deuterium cannot be produced in significant quantities in stars. (If it could, this would be a great disappointment to cosmologists.) On the other hand, deuterium burns very easily and significant cycling of cosmic material through stars ought to lead to its depletion. It is therefore significant that millimeter-wave observations of deuterated molecules in interstellar clouds indicate a greater depletion of deuterium toward and in the galactic center region. This depletion provides observational evidence

TABLE 1.– ORIGIN OF THE CNO ISOTOPES

Isotope	Relative abundance (atomic) in solar system	Synthesis	Means of ejection to the ISM[a]
^{12}C	1500	Helium-burning	SN,RG/PN
^{13}C	17	Equilibrium CNO	RG/PN
^{14}N	480	Equilibrium CNO	RG/PN
^{15}N	1.8	Hot CNO	N
^{16}O	2800	Helium-burning	SN
^{17}O	1.0	Equilibrium CNO Hot CNO	N
^{18}O	5.5	Helium-burning	SN

[a]SN = supernovae
RG = red giants
PN = planetary nebulae
N = novae

against galactic production of deuterium, and supports a cosmological interpretation. The best determination of D/H in the interstellar medium comes from UV observations of the Lyman bands of molecular and atomic hydrogen and deuterium; these yield D/H = 1.8 $\pm 0.4 \times 10^{-5}$, consistent with physical conditions in the Big Bang inferred by independent means.

Hydrostatic Hydrogen-Burning: the CNO Cycles

The accepted scenario for the production of the CNO elements is as follows. Hydrogen and helium from the Big Bang form a first generation of stars in which, after proton-proton hydrogen-burning, ^{12}C forms by the triple-alpha process, and subsequently ^{16}O forms by helium-burning. These nuclides, ^{4}He, ^{12}C, and ^{16}O, are generally regarded as primary nucleosynthetic products, since they can form in first-generation, metal-poor stars. There is evidence that in some stars deep mixing may bring primary carbon and oxygen up to the hydrogen-burning zone. In such cases, products of CNO processing such as ^{14}N may also be primary in nature. When primary CNO nuclei are incorporated into second-generation stars, hydrogen-burning may be accomplished by the catalytic CNO process described below.

In stars containing carbon, nitrogen, or oxygen nuclei at the outset, ^{1}H can burn to form ^{4}He by an alternative mechanism, the CNO process. The carbon, nitrogen, and oxygen nuclei effectively act as catalysts for hydrogen-burning. The abundances of the CNO nuclei are altered in the process. The most important range of stellar masses for catalytic CNO processing is 3-6 solar masses ($M_\odot$), too small for supernovae but massive enough to have extensive CNO processing occur in them. In such stars the mass lost to the ISM comes from the outer envelope, producing planetary nebulae and dense circumstellar clouds. The nuclear processes that are important in these stars depend on the stellar mass, the mass of the expelled envelope (i.e., the depth to which it extended in the star), and the amount of mixing that occurred within the star prior to expulsion of the envelope.

There are actually three interlocking catalytic CNO cycles that are important astrophysically. These are interconnected at two important "branching points." CNO processing is said to produce "equilibrium" abundances when it proceeds at a rate slow compared to the several beta decays involved in the reaction cycles. In this case, the proportions of the isotopes are determined by their relative cross sections for proton capture.

The measured nuclear cross sections of the CNO cycles imply the production, in equilibrium, of an overwhelming amount of ^{14}N. This product, in combination with ^{12}C and ^{16}O from primary processing, is responsible for the abundances of the principal isotopes of C, N, and O. Subsequent proton captures by ^{12}C, ^{14}N, or ^{16}O are each followed by a beta decay which occurs at a fixed rate. Thus, if hydrogen-burning could be interrupted then the odd nuclei ^{13}C, ^{15}N, or ^{17}O would be enhanced. Such nonequilibrium or incomplete burning may occur as a result of quick quenching or burning material in novae, or in supernovae in the outward shock. A similar enrichment occurs in the envelopes of giant stars. The odd nuclei, though rarer than the even nuclei, have sufficiently large cosmic abundances to imply a significant enrichment by incompletely processed material.

Independent of the site of CNO processing or the experimental values of the branching ratios, a few trends are predictable. The abundances of those isotopes that are secondary products of nucleosynthesis can be expected to increase with time relative to primary products, which can be produced in first-generation, low-metal stars. Assuming an initial CNO composition that is approximately solar, the CNO nuclei will become rearranged by equilibrium burning to produce ^{14}N (increasing N/H), especially at the expense of oxygen (increasing N/O). Although the total abundance of carbon is decreased by equilibrium processing, ^{13}C is enhanced, and in the steady state situation this yields $^{12}C/^{13}C \sim 4$ (a decrease of $^{12}C/^{13}C$). Strong observational support for operation of the catalytic CNO process comes from observed abundances in the atmospheres of red giants, and from recently expelled material. Observed carbon isotope ratios, for example, range from the terrestrial value of $^{12}C/^{13}C = 90$ to the CNO process equilibrium value of 4.

To the extent that nonequilibrium CNO processing is important, ^{13}C is also enhanced, as are ^{15}N and ^{17}O. The predicted evolutions of

$^{14}N/^{15}N$ and $^{18}O/^{17}O$ are somewhat obscure. Initial ^{15}N certainly forms ^{14}N by the equilibrium CN cycle (in giants), but ^{15}N is also formed explosively from ^{14}N in novae. The evolution of $^{14}N/^{15}N$ thus depends on the relative importance of novae (or supernovae) and of equilibrium burning in stars. The time evolution of $^{14}N/^{15}N$ may therefore reflect the evolution of the stellar population. $^{18}O/^{17}O$ is also difficult to model, because of the somewhat uncertain values of an important branching ratio at ^{17}O in the CNO cycles and because ^{18}O is formed mostly by helium-burning under conditions very different from those that apply to CNO processing. The most important processes are summarized in table 1.

Synthesis of the Heavy Elements

Beyond the CNO elements, sulfur and phosphorous are probably of the greatest biological importance; perhaps also magnesium and iron. Of the nuclides beyond atomic weight 18, it is thought that only ^{22}Ne can be formed by the hydrogen-burning and helium-burning reactions already discussed. The other heavy nuclides are formed either by advanced quiescent burning in massive stars that have nearly exhausted their nuclear fuel, or by explosive burning in supernovae. The nuclides ^{12}C and ^{16}O, which are formed by the triple-alpha reaction, can combine in massive stars to form ^{24}Mg or ^{32}S at temperatures corresponding to ~100 and ~200 keV, respectively. These reactions are logically the next in a chain of orderly burning processes. However, the actual production of the nuclides in the mass range 24 to 44 is complicated by the fact that oxygen and silicon burn at temperatures so high that photodisintegration becomes an important process. As a result, small nuclear fragments are produced, and the reaction pathways available become rather complex. In the resulting network of reactions, the relative isotope abundances are sensitive to the exact ratio of neutrons to protons in the fuel. Thus the initial abundance of neutron-rich CNO nuclides has an important effect on the production of neutron-rich nuclei of the heavier elements.

It should be noted that after carbon-burning, the time scales associated with the more advanced burning processes can be shorter than the dynamic time scales of massive stars, so that it is difficult to visualize these processes happening quiescently. Despite all the difficulties associated with the modeling of advanced stellar nucleosynthesis, certain features of the terrestrial abundance ratios can be reproduced. The observed proportions of the sulfur isotopes, for example, can be understood from the known reaction cross-sections. Because all this burning happens in massive stars, even the products of "quiescent" burning are subsequently modified by explosive burning during the imminent supernova.

EJECTION OF PROCESSED MATERIAL INTO THE INTERSTELLAR MEDIUM

The nucleosynthetic processes described above become important for the inventory of biogenic elements only if and when the processed material is ejected into the ISM, so that the newly formed elements can be incorporated in subsequent generations of stars and their accompanying planets. The processed material is returned to the ISM by a variety of mass-loss phenomena. Mass-loss from stars has been intensively studied by astronomers working in all portions of the electromagnetic spectrum. Mass-loss is associated with all stages of stellar evolution, but the phenomena of greatest significance for the present discussion occur in the late (post-main sequence) stages of the life of a star. The importance of the mass-loss can be seen from the fact that white dwarfs and neutron stars, which are thought to be the endpoints of stellar evolution, are observed to have masses $\leqslant 2M_{\odot}$, while main sequence stars have masses as large as 30 to 50 $M_{\odot}$. Much of this mass must therefore be returned to the ISM during the stars' lifetimes.

For stars less massive than ~5 $M_{\odot}$, the mass-loss occurs gradually, as the post-main sequence stars pass through the red giant and planetary nebula stages. More massive stars undergo supernova explosions in which much of the stellar mass is returned to the ISM in one violent episode. The nature of these phenomena and their importance for the addition of newly synthesized biogenic elements to the ISM is summarized below.

Supernovae

A supernova explosion results in the destruction of an entire star, and may eject tens of solar masses of material to the ISM at velocities in excess of 5000 km/sec. The total energy released almost instantaneously in a supernova explosion can be in excess of 10^{51} ergs, equal to the energy radiated by the Sun in 10^{10} years. The peak luminosity of a supernova often approaches 10^{10} times the current luminosity of the Sun, so that a supernova can be momentarily brighter than an entire galaxy of stars. The frequency of supernova explosions in a galaxy such as our own is estimated with considerable uncertainty to be one every 50 yr. It is believed that the explosion is triggered by the release of gravitational energy as the stellar core is transformed into a neutron star.

Supernovae are thought to be the principal stellar sources of ^{12}C, ^{16}O, and all more massive elements, and to contribute significantly to the ^{14}N abundance as well. Elements more massive than neon, and some rare isotopes of the lighter elements, are created by explosive nucleosynthesis in the actual supernova event. The more abundant isotopes ^{12}C and ^{16}O are synthesized in equilibrium processes in the outer core of the presupernova star, and are ejected to the ISM by the supernova explosion. A typical calculation shows that a supernova explosion in a 22 $M_\odot$ star returns 7 $M_\odot$ of newly synthesized elements, including 3 $M_\odot$ of He, 1 $M_\odot$ of C, 0.1 $M_\odot$ of N, and 1.3 $M_\odot$ of O, plus additional heavier elements, to the ISM.

The role of supernovae as suppliers of heavy elements is dramatically illustrated by the supernova remnant Cassiopeia A (Cas A), originally discovered as the strongest radio source in the sky but subsequently studied in the IR, optical, and X-ray spectral bands. Cassiopeia A appears to be the remnant of a supernova that occurred about 300 yr ago. The optical observations show rapidly moving knots of gas which contain little or no hydrogen, but are rich in heavy elements such as oxygen, calcium, and sulfur; these fast-moving knots appear to be highly enriched material from within the star that was accelerated and ejected during the supernova explosion. X-ray observations of Cas A show that the knots are embedded in a hot plasma that shows considerable overabundances of silicon, sulfur, argon, and calcium.

Novae

Novae are stellar explosions that are more frequent, but much less dramatic, than supernovae. Typical peak luminosities are 10^4-10^5 $L_\odot$, and the total mass ejected is $\sim 10^{-4}$ $M_\odot$. ($L_\odot$ = the solar luminosity.) The rate of occurrence of novae in the galaxy is ~10/yr. It is believed that novae occur in binary star systems consisting of a primary star, moderately evolved, which is losing mass slowly, and a more evolved white dwarf companion. Some of the mass lost by the primary star is accreted onto the white dwarf. The accreted material accumulates until it is hot and dense enough for nuclear reactions to occur; the resulting energy release leads to a thermonuclear runaway which produces the nova outburst.

For certain classes of novae, observations and theory suggest that the surface layers of the white dwarf secondary are rich in CNO. In these cases, the nuclear reactions occurring are similar to those associated with the CNO cycles in stellar interiors, but the various CNO isotopes are produced in very different relative amounts because physical conditions and time scales for the nova explosion are very different from those in a stellar interior at equilibrium. Thus while novae are not as important overall for the production of CNO as are the other sites discussed here, they are believed to be the main sources of some of the rarer CNO isotopes, such as ^{15}N and ^{17}O.

Red Giants

Red giants are luminous ($L > 10^4$ $L_\odot$) cool ($T < 3000$ K) stars that eject processed material into the ISM via stellar winds. They are less dramatic than the supernovae and novae, but mass-loss rates in excess of 10^{-5} $M_\odot$/yr, very high by astronomical standards, are common in red giants. Since the total mass lost by such a star is more than 2 $M_\odot$, the red giant phase is of moderately long duration, making such objects quite common, so that they account for perhaps 0.1% of all stars in the solar neighborhood. The red giants were originally identified and classified by optical observations. Recently, IR and

radio observations have made possible the detection of red giants at distances of more than 10 kpc in the galactic plane. This is far beyond the range of optical observations, which are restricted by interstellar absorption.

Red giants and their winds play several roles in the galactic budget of biogenic elements. Their atmospheres and winds show evidence for values of the $^{13}C/^{12}C$ ratio as high as 1/6, much greater than the solar value of 1/90 and the local interstellar value of 1/60. This shows that the red giant atmosphere contains material which has undergone partial CNO processing in the stellar interior, and red giants are thought to be the principal sources of ^{13}C and ^{14}N, the isotopes that are enhanced in equilibrium CNO processing.

The role of red giants in nucleosynthesis is even more dramatically demonstrated by the fact that large numbers of these stars show C/O ratios greater than unity, in marked contrast to the solar and local interstellar value (C/O = 0.55). One of the best-studied of these carbon stars is IRC+10216, which has a molecular shell with a total mass of more than 2 $M_\odot$, and a current mass-loss rate of 10^{-4} $M_\odot$/yr. The enhanced $^{14}N/^{15}N$ and $^{13}C/^{12}C$ ratios determined for the molecular shell by radio and IR observations provide evidence of material that has undergone cold CNO processing, as mentioned above. Additionally, the fact that $C/O > 1$ and C/H exceeds the solar system value implies that some of the material in the atmosphere has been dredged up from even deeper layers within the star, where carbon is being synthesized by the triple-alpha process. Thus in IRC+10216 we find evidence for the products of two different nuclear burning processes. Note that the effect of the CNO cycle is to change the relative numbers of the various CNO isotopes, whereas the carbon produced by the triple-alpha process increases the total number of CNO nuclei.

Planetary Nebulae

Planetary nebulae are dense shells of hot gas, ionized and excited by very hot stars. The shell masses are $\gtrsim$0.2 $M_\odot$. About 1000 planetary nebulae have been identified optically, and have been studied by a range of IR, optical, and UV techniques that have concentrated on determining the abundances of the elements in the gas. Several objects with properties intermediate between red giants and planetary nebulae are known. It is therefore believed that planetary nebulae are formed in the final stages of the evolution of a red giant, when the last layers of the star are blown off to unmask an underlying hot dwarf. Since the gas in a planetary nebula comes from deep within the parent star, it can be expected to have undergone appreciable nuclear processing. Enhanced abundances of He, C, and N have been reported for planetary nebulae.

The State of the Ejected Material

The nucleosynthesis sites described above eject gas to the ISM in a wide variety of physical states, ranging from the hot plasma of the supernova remnants to the cool molecular shells of the red giants. The same stellar objects are also extremely important as sources of dust grains, which constitute only ~1% of the ISM by mass but are composed entirely of heavy elements. The dust grains are an important component of the biogenic element picture for many reasons: They are the principal reservoir of heavy elements in the ISM; they are important sites for both the formation and the depletion of interstellar molecules (chapter IV), and shield newly formed molecules from dissociation by starlight; they provide the major source of radiative opacity in a collapsing interstellar cloud within which stars and planets may form (chapter V); they respond to the interstellar environment and carry with them the record of their origins in different ways than does the gas. Thus the anomalies in stable isotope abundances identified in meteorites may have been carried intact to the nascent solar system by grains that were formed in supernovae.

The condensation of grains has been observed in association with each of the phenomena described above: supernovae, novae, red giants, and planetary nebulae. The association of grains with mass-loss in red giants is particularly instructive. Red giant stars with high mass-loss rates are surrounded by very thick dust shells of their own manufacture. These shells extinguish most of the visible light emitted by the underlying stars, but reradiate the star's energy at wavelengths around 10 μm, so that objects of this class are very bright in the IR. It appears that

radiation pressure on the circumstellar dust is important in accelerating the stellar winds to their terminal velocities, although it is not clear whether the dust grains actually cause the mass-loss or just condense in the outflowing material. The distinction between carbon- and oxygen-rich red giants which can be made from observations of their gaseous composition is borne out by IR studies of the dust they synthesize. These studies suggest that the carbon-rich stars have dust composed of materials similar to graphite or silicon carbide, whereas the oxygen-rich stars have dust composed of silicate minerals.

Although definite numbers are lacking, it is clear that an important fraction of the newly synthesized biogenic elements may be ejected into the ISM in the form of dust rather than gas. In the case of the planetary nebula NGC 7027, for example, it is estimated that carbon is enriched relative to hydrogen by a factor of 6, and that about half of the excess carbon is in the form of graphite-like grains.

UNSOLVED PROBLEMS AND RESEARCH OPPORTUNITIES

There are several areas of experimental, observational, and theoretical study that can provide additional insight into the origin of biogenic elements. The evolution of the heavy elements depends strongly on nucleosynthesis and mass-loss during very late stages of stellar evolution. Models of these stars are difficult to construct, in part because the stars can have very complex structures. Nuclear burning rates are quite important, and these are often not known with sufficient accuracy at the temperatures in question. Because our understanding is at present insufficient to predict abundances accurately in mass-loss objects, observations are doubly important. First, extensive observations of a few objects can provide tests for stellar models and thus can sharpen our theoretical tools. Second, surveys of many objects can provide a general picture of the types of enrichment attributable to each class of stellar objects.

Observational Studies

The important sources of processed material are supernovae, novae, and red giant mass-loss, including circumstellar shells and planetary nebulae. It is clear from existing observations of circumstellar shells that late-type stars can display a great diversity of elemental abundances. This diversity is presumably a result of differences in initial stellar mass and composition, as well as other properties, such as rotational velocity and the presence or absence of a binary companion. Although there are relatively few observations of abundances in nova and supernova ejecta, it is expected that these objects will also display a diversity of abundances. It is therefore essential to survey a representative sample of objects, not merely a few prototypical objects.

For the study of quiescent mass-loss, visible red giants, circumstellar shells, and planetary nebulae are all profitable targets of research, and may represent different stages of evolution in similar objects. Infrared surveys, if made with sufficient sensitivity, might be used to measure the sum total of mass-loss by late-type stars in our galaxy. In circumstellar shells, isotope abundance measurements can be made at millimeter and IR wavelengths, and the available techniques can certainly be exploited to a much larger extent than they have been to date. High-resolution millimeter-wavelength interferometers will undoubtedly contribute to studies of circumstellar shells, all of which seem to show very significant structure at sizes smaller than existing single telescope beam widths. The information available from IR absorption-line observations indicate asymmetries and irregularities in the mass outflow which, when supplemented by millimeter-wave emission measurements at high resolution, is certain to shed light on the mass-loss mechanism in these objects. Observations of supernovae and supernova remnants can be made in the most straightforward way by optical and high-resolution UV line spectroscopy. Spectra of developing (optically thick) supernovae in other galaxies will provide information about the physics of early supernova expansion, especially when the supernovae have been caught early enough to study their time development. The ionized gas in older remnants can provide information about the composition and structure of the exploding object. High spatial resolution will be helpful in detecting compositional differences among the fragmentary debris of recent remnants. In addition to direct observations of supernovae and their remnants, detailed

abundance measurements in cosmic rays can provide additional information about nucleosynthesis in supernovae, even though the cosmic rays cannot be associated with a specific supernova. Several recent satellite-borne instruments have been effective in this regard, and more observations with high mass-resolution would be helpful.

Observations of novae are in a somewhat undeveloped state, although these objects are especially important for the production of certain of the CNO isotopes. Infrared and millimeter methods may eventually provide abundance information, especially since recent results indicate the presence of dust and molecular gas in the expelled material. One of the difficulties will be to get the observational scheduling flexibility to be able to study promising events when they occur.

To learn more about star formation and nucleosynthesis will require observations of interstellar abundances in our galaxy and in other galaxies. Millimeter-wave and far-IR spectra can provide isotope abundance information that is relatively insensitive to interpretational uncertainties. Good IR observations are still difficult to make, pending the development of orbiting observatories with adequate spectral resolution. For both the millimeter and IR extragalactic observations, there is a need for high spatial resolution.

Theoretical Studies

The gathering of astronomical data cannot by itself remove all the major obstacles that currently limit our understanding of nuclear production. Most of the heavy element synthesis occurs in very late stages of stellar evolution, where present stellar models are the least reliable. Models have improved substantially because of their increasing numerical sophistication, and this trend is bound to continue. However, there are serious limits to our physical understanding which limit the accuracy of any model. As mentioned earlier, nuclear production depends sensitively on the extent of mixing provided by convection in evolved stars. Unfortunately, convection is a particularly difficult topic to treat in late-type stars, which can have several burning zones and corresponding inhomogeneities in chemical composition.

Models of the outer stellar layers, which give rise to the mass-loss phenomenon, will also have to be improved. At present, only the evolution of stellar cores is understood with any confidence. In addition to the static phases of stellar evolution, it is necessary to understand more completely the phenomena in the explosive phases. Much of the nucleosynthesis and ejection of the heavy elements takes place in novae and supernovae, yet our physical understanding of these events is far from adequate to permit the prediction of resulting abundances to within factors of 2. Some of the uncertainties result from a lack of adequate laboratory data on nuclear reaction rates; indeed, some important recent breakthroughs have resulted from improved measurements of reaction cross-sections at suitably low energies.

The final step to understanding the production of the biogenic elements will be to incorporate the information we have about specific stellar objects into a global model of nucleogenesis on a galactic scale. This model must take into account the changing proportions of stellar nucleosynthesis sites over the lifetime of the galaxy, in order to understand the present-day pattern of elemental abundances in the interstellar medium.

Additional Reading

Audouze, J.; and Tinsley, B. M.: Chemical Evolution of Galaxies. Ann. Rev. Astron. Astrophys, vol. 14, 1976, pp. 43–79.

Iben, I., Jr.: Post Main Sequence Evolution of Single Stars. Ann. Rev. Astron. Astrophys., vol. 12, 1974, pp. 215–256.

Pagel, B. E. J.; and Edmunds, M. G.: Abundances in Stellar Populations and the Interstellar Medium in Galaxies. Ann Rev. Astron. Astrophys., vol. 19, 1981, pp. 77–113.

Tinsley, B. M.: Evolution of the Stars and Gas in Galaxies. Fund. Cosmic Phys., vol. 5, 1980, pp. 287–388.

Trimble, V.: The Origin and Abundances of the Chemical Elements. Rev. Mod. Phys., vol. 47, 1975, pp. 877–976.

Wannier, P. G.: Nuclear Abundances and Evolution of the Interstellar Medium. Ann. Rev. Astron. Astrophys., vol. 18, 1980, pp. 399–437.

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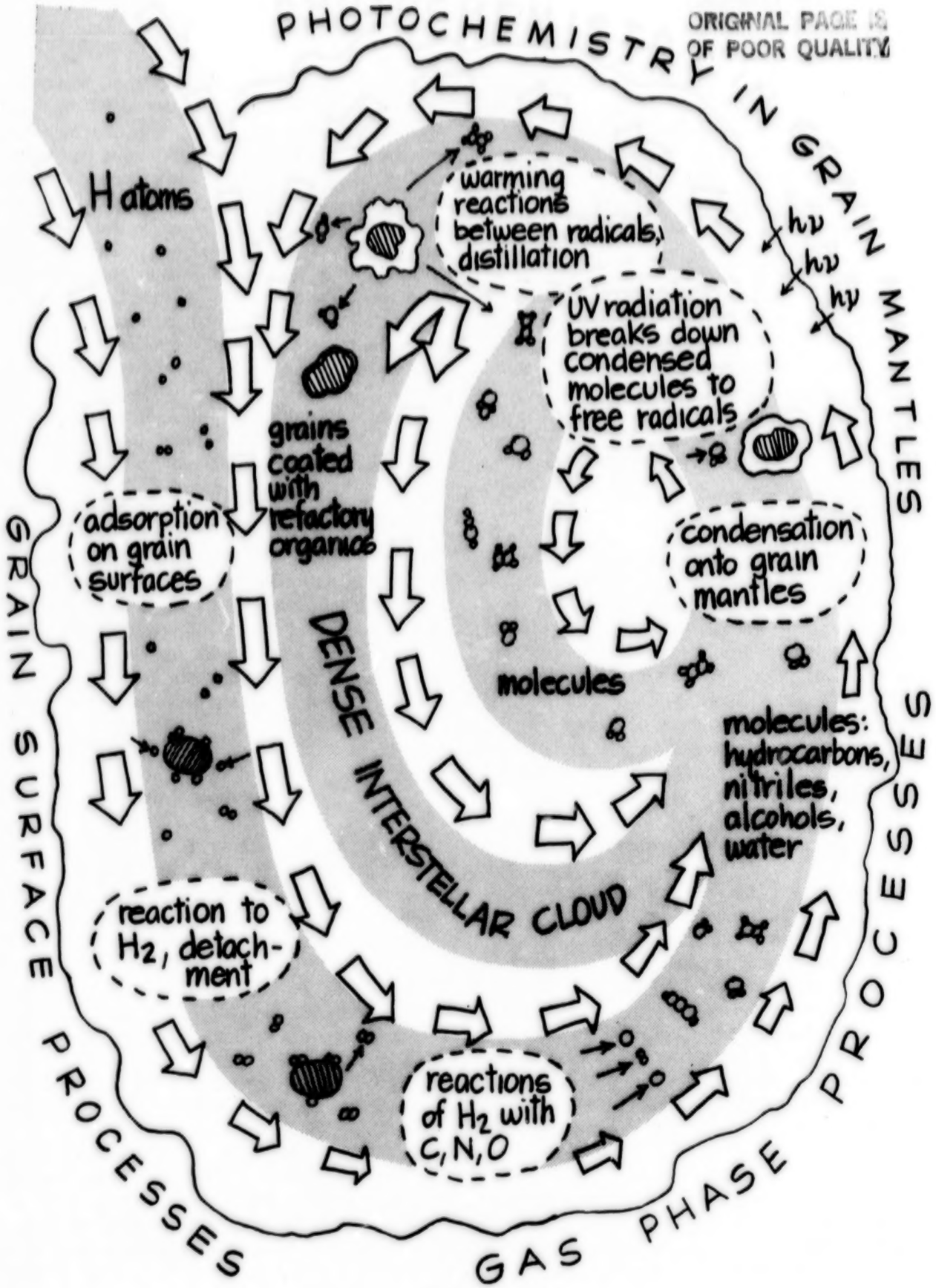

Figure 3.

IV

Chemical Evolution in the Interstellar Medium

Atoms of the biogenic elements combine to form molecular species, both gaseous and condensed, in regions of space called absorption (dark) nebulae or interstellar clouds. These clouds, which are light years in extent and occupy ~5% of the galactic volume, contain both a gas phase and a solid phase. The solid phase consists of dust particles about 0.1 μm in size, and typically constitutes ~1% of the cloud mass. The elemental composition of the gas and dust reflects the well-known cosmic abundances of the elements, in which the number ratio of (C+N+O)/H is about 0.001. Some depletion of the carbon, nitrogen, and oxygen from the gas phase is well observed, and one can estimate that 20% or more of the atoms of these elements must have condensed to the solid phase.

In the discussion here, we separate interstellar clouds into two classes: diffuse clouds, which generally have mostly atomic rather than molecular hydrogen; and dense clouds, in which the hydrogen is overwhelmingly molecular. A rough dividing line between the two occurs where the optical extinction due to dust is equal to unity.

DIFFUSE INTERSTELLAR CLOUDS

In the diffuse clouds, which can be studied by the line absorption of background visible and UV stellar radiation, gas densities do not exceed several hundred atoms/cm^3; gas temperatures are 50-100 K; dust temperatures are ~10 K; and the gas is mainly atomic and shows depleted cosmic abundance ratios. These clouds were first studied in the visible over 40 yr ago, and the gas phase spectra of the transient molecular species CH, CH^+, and CN were assigned. However, most stable molecular species have their electronic spectra in the UV. In the last decade, rockets, and more importantly satellites such as Copernicus, have carried spectrometers that showed diffuse clouds to contain substantial amounts of gaseous CO and H_2.

In some of the denser diffuse clouds, the molecular hydrogen and atomic hydrogen abundances are roughly similar. Diffuse clouds also display a number of diffuse absorption features in the visible which may be due to complex organic gas phase molecules, or to molecules in the dust grains. These features have been known and unassigned for many years. A detailed attack on the sources of these spectra is warranted. The continuum extinction by dust grains of stellar radiation as it passes through diffuse clouds can be simulated by a variety of substances. Among these is an amorphous silicate material which produces a broad absorption feature in the IR. However, cosmic abundance limitations on silicon require that the major contribution to the continuum extinction be produced by the biogenic elements. Indeed, it is required that a number of different kinds of absorbing dust grains exist. For example, to explain a bump that the extinction pattern displays at 2160 Å, one is led to consider absorption by some sort of carbon particles whose characteristic size is smaller by a factor of 10 than those particles that provide the visible extinction.

Infrared work on warmer regions, where the dust grains produce emission features, and in the direction of the galactic center, which provides enough total extinction to bring out absorption features, show great promise of helping to specify the grain compositions.

DENSE INTERSTELLAR CLOUDS

Study of the dense clouds, which are opaque in the visible and UV, has become possible in the last 15 yr by means of IR and "radio" astronomical techniques. The word "radio" here refers to microwave, millimeter, and submillimeter observations. These longer wavelengths are less effectively absorbed and scattered by the dust than are visible and UV radiation. Most important have been the microwave observations, which have detected more than 50 gas-phase molecular species (table 2). These molecules are typically observed in emission against the universal 3 K blackbody background, at microwave or millimeter frequencies corresponding to rotational quantum transitions. Table 2 contains an up-to-date list of known interstellar molecules, observed principally in dense clouds. Most of these species can be categorized as organic or carbon-containing; the most complex molecule yet reported is an 11-atom species, HC_9N. The fraction of biogenic elements occurring in the aggregate of the detected gaseous molecules is about 25% of that which is in the dust.

The properties of the dense clouds have been deduced most effectively from radio telescope maps of a few molecular transitions, especially the 2.6-mm line of CO and its isotopic variations. These clouds range from the small dark nebulae and Bok globules of diameter less than 1 ℓy to the giant molecular clouds 100 ℓy across. The latter contain up to one million solar masses of gas, and are therefore probably the largest gravitationally bound units in the galaxy. The temperatures and gas densities in the envelopes of these clouds are typically 5–10 K and 10^3–10^4 H_2 molecules/cm^3, respectively, but in the cloud cores observed temperatures are at least 100 K and densities greater than 10^6 H_2 molecules/cm^3 are often estimated. Finer spatial resolution in the radio studies, were it available, would probably reveal even hotter, denser gas. It is these core regions that are the sites of current star and planetary formation. Indeed, near-IR continuum measurements often show embedded luminous stars clustered in them. In a few instances (e.g., the Orion cloud core) recent studies have revealed highly supersonic shock waves which raise the gas temperature above 1000 K.

The gas phase of dense clouds is now known to consist chiefly of molecular hydrogen. Some additional abundant species are carbon monoxide (fractional abundance, 10^{-4}) and water (10^{-5}), both with respect to H_2. Other molecules have fractional abundances significantly lower than these. Still, the amount of matter in the form of each detected biogenic molecule is exceedingly large, because of the vastness of many of the dense molecular clouds. Ethanol is a trace species in most clouds, with a fractional abundance of 10^{-10} of the gas density. Nevertheless, for a cloud of 1000 solar masses, the mass of ethanol alone is comparable with the

TABLE 2.– MOLECULES OBSERVED TO DATE IN THE INTERSTELLAR MEDIUM[a]

H_2, CH, CH^+, CN, CO, CS, OH, SiO, NS, SO, SiS, NO, CO^+, HCℓ
H_2O, H_2S, HCN, HCO^+, HCO, HNC, HN_2^+, CCH, OCS, SO_2, HNO, HCS^+, COH^+
NH_3, H_2CO, H_2CS, HNCO, CCCN, HNCS, HCCH, CCCO
CH_4, CH_2CO, CCCCH, H_2CNH, H_2NCN, HCOOH, HC_3N, SiH_4
CH_3OH, CH_3CN, $HCONH_2$, CH_3SH, C_2H_4
CH_3NH_2, CH_3CCH, CH_3CHO, C_2H_3CN, HC_5N
$HCOOCH_3$, CH_3CCCN
CH_3OCH_3, CH_3CH_2OH, HC_7N, CH_3CH_2CN, CH_3CCCH
HC_9N
$HC_{11}N$

[a]Includes IR observations of circumstellar sources (CH_4, C_2H_2, C_2H_4, SiH_4) and a microwave observation ($HC_{11}N$) of such a source.

mass of the Earth, while the mass of the biogenic elements in the dust is ~3 $M_\oplus$!

Infrared spectroscopic studies of the dense interstellar clouds are aimed at regions with background continuum sources (protostars), on which the absorption spectrum of intervening cloud material can be read. These studies can probe both the gas and solid phases of clouds. Gaseous molecular densities and temperatures under most cloud conditions are insufficient to excite IR line emission. Infrared absorption studies involve transitions between the vibrational levels of molecules. It is unclear how similar the chemistry of these warm regions is to that of the ambient interstellar gas. Infrared studies are particularly valuable for the study of those gaseous molecules without a permanent dipole moment, as these species do not possess strong spectra at lower frequencies. Some important examples of nonpolar species with electric dipole IR spectra are carbon dioxide, ozone, and all basic hydrocarbons. In addition, electric quadrupole IR spectra of H_2 have been detected.

Infrared observations of grains in various astronomical regions have revealed a wide variety of spectral features, with relative strengths that vary considerably from one object to another. The water ice band at 3.1 μm has received considerable attention. Its optical depth as well as its shape have important consequences for our understanding of grain mantles. Other, less pronounced, features are becoming increasingly identifiable and should ultimately provide a key to the chemical constituents and evolution of grains in clouds.

Most of the molecules observed in dense clouds are well known from terrestrial spectroscopic studies. This is because astronomers typically search for frequencies already studied in the laboratory. Occasionally, astronomers detect spectra that cannot be assigned to known molecules, which they label "U" (unidentified) lines. These U lines are sometimes identified by a combination of quantum chemical and other theoretical techniques. However, laboratory confirmation is required for unambiguous identification. The history of the transient molecular ion HCO^+ provides an example. The initial discovery of an unidentified line at 89.190 GHz was followed by a suggestion, based on an understanding of cloud chemistry, that the carrier was HCO^+. Quantum chemical investigations were in agreement with this suggestion, but were not accurate enough to provide unambiguous confirmation of the assignment. Eventually, the laboratory spectrum of the ion HCO^+ was achieved, which confirmed the initial assignment.

Because 100-300 unidentified lines are now known, more laboratory spectroscopic studies of likely transient species are needed, as are more detailed quantum chemical calculations. It is unclear, however, that all of the U lines are due to transient species that are hard to produce in the laboratory. The laboratory spectra of even the most standard of organic molecules are poorly worked out in the millimeter and submillimeter spectral regions, which are the most sensitive for astronomers. Thus, laboratory studies of both stable and transient species in these regions of the electromagnetic spectrum are needed.

Recent observations of molecules in dense clouds indicate that in the older clouds, gaseous molecules are probably being depleted by condensation onto the surfaces of the dust grains. Thus, much of the biogenic matter may well be on and in the grains. It is these grain materials that may eventually accrete into planetesimals during periods of star formation (chapter VII) in cloud cores. Infrared astronomers have recently observed a variety of broad spectral features that are due to dust. It is to be hoped that an understanding of the origin of these features will lead to an understanding of the nature of the grains.

THE FORMATION OF MOLECULES

Where are gaseous molecules formed? In the clouds themselves, or in external sources? Simplicity suggests that, unless there is strong evidence to the contrary, *in situ* formation mechanisms should be sought. External sources do have some appeal, however, because regions with higher densities and temperatures, which are normally thought to be more conducive to molecular development, can be considered. External regions such as red giant stellar atmospheres and novae are known to evolve and eject dust particles. In addition, some of the same complex molecules seen in interstellar clouds are also detected in circumstellar sources such as

IRC+10216. Nevertheless, it must be recalled that high-temperature and high-pressure sources also exist inside dense clouds in the form of protostars, and need not be "external" at all.

Up to the present, astrophysicists and astrochemists have devoted most of their attention to detailed low-pressure, low-temperature *in situ* formation mechanisms. Some of the reasons for this preference are:

1. The interstellar molecules display a degree of D/H chemical isotopic fractionation that requires $T \ll 100$ K.
2. Rapid *in situ* reactive depletion processes tend to destroy interstellar molecules. The observed gaseous molecular abundances must be an approximately steady-state population, requiring that the molecules are continually being formed.
3. Gaseous molecules would be destroyed by photodissociation unless they are continuously shielded from UV radiation during the journey from an external source to an interstellar cloud.
4. It is difficult to fit observed molecular abundances to high-pressure, thermodynamic models, unless the source is carbon-rich.

More detailed quantitative models of "external" sources should be undertaken, to see if the above objections are indeed compelling. One possibility is the formation at high pressures of some complex molecules on high-temperature catalytic grain sites, followed by spallation from the grains in the dense cloud environment.

The three major mechanisms of *in situ* molecule formation from primeval atoms are gas phase processes, processes on the surface of dust grains, and photochemical processes in the solid grains themselves. These mechanisms are shown interacting in figure 3. This sketch is highly schematic, however. We stress that the true situation is far more complex and less well understood than is suggested by this drawing.

Gas Phase Processes

Gas phase processes are severely restricted by the low ambient temperatures and pressures to binary collision events which require little or no "activation" energy. Most chemical reactions involving stable molecules fail this criterion, because energy is required to break old chemical bonds before new ones can be formed even if the overall process is exothermic (releases energy) rather than endothermic (absorbs energy). Measured exceptions to this rule are exothermic reactions between atoms and transient neutral molecules (free radicals) and, more important, exothermic reactions between positively charged molecules (ions) and neutral species or electrons. These latter reactions are thought to be dominant in interstellar clouds, and to synthesize polyatomic molecules once there are significant amounts of diatomic molecules. The major processes producing ions are cosmic ray bombardment and, in diffuse clouds not opaque to UV radiation, UV photoionization. "Normal" chemical reactions of the type

$$A + B \rightarrow C + D$$

(where A, B, C, and D are atoms or molecules) can synthesize polyatomic molecules from diatomic species, but cannot explain how primeval atoms combine to form diatomic molecules. The process invoked – radiative association – involves the collision of two atoms (A and B) to form a temporary "collision complex" AB*, which can radiate away enough energy to survive and stabilize itself:

$$A + B \rightarrow AB^* \rightarrow AB + h\nu$$

Such a process is inefficient for even the most favorable atomic collision partners. For example, the radiative association of carbon ions and hydrogen atoms is calculated to take place in one out of every 10^8 collisions. The radiative association of two hydrogen atoms to form a hydrogen molecule is orders of magnitude more inefficient than this, and is far too slow to produce the observed concentration of molecular hydrogen in clouds. For the synthesis of this important species, recombination of hydrogen atoms on dust grains must be invoked.

Using the above processes, astrophysicists have constructed quantitative chemical models of diffuse and dense clouds. In dense cloud models, gas phase chemical reactions both produce and destroy all molecules except for molecular hydrogen, the formation of which occurs on grain surfaces. It is instructive to see how a relatively abundant molecule – water – is both created and destroyed in these models. The sequence of reactions is as follows:

$$H_2 + \text{cosmic ray protons} \rightarrow H_2^+ + \text{electron}$$

$$H_2^+ + H_2 \rightarrow H_3^+ + H$$

$$H_3^+ + O \rightarrow OH^+ + H_2$$

$$OH^+ + H_2 \rightarrow OH_2^+ + H$$

$$OH_2^+ + H_2 \rightarrow OH_3^+ + H$$

$$OH_3^+ + \text{electron} \rightarrow H_2O + H, OH + H_2$$

$$H_2O + \text{ions} \rightarrow \text{products}$$

Cosmic rays ionize molecular hydrogen. The resulting ion reacts with hydrogen to form the triatomic molecular hydrogen ion, which can react with a variety of primeval atoms including oxygen. A series of subsequent ion-molecule reactions then produce the stable molecular ion OH_3^+, which recombines with electrons to form both the stable species water and the transient hydroxyl radical OH. Although ion-electron recombination reactions have been studied in the laboratory, the branching ratios between possible products have not yet been determined. Work on this important subject should be undertaken.

In diffuse cloud models, the destruction of most molecules is dominated by rapid photo-induced processes which severely limit molecular development. The accuracy of such models is limited, however, by the lack of laboratory studies on photodissociative cross sections in the UV. An example is the uncertain photodissociation rate of carbon monoxide, which renders predictions of the abundance of this species in diffuse clouds highly uncertain.

Both steady-state and time-dependent models of the gas phase chemistry of dense and diffuse interstellar clouds have been undertaken. In general, the models satisfactorily reproduce observed interstellar molecular abundances of the smaller (2-4 atom) species, but do not account well for the larger species. Even among the smaller molecules, there are some notable discrepancies between calculated and observed abundances. The CH^+ abundance in diffuse clouds can be accounted for only by assuming severe cloud heating caused by the passage of supersonic shock waves. This heating would permit a wider variety of gas phase reactions to occur. Evidence for the action of shock waves is rather strong; the effect of shock-wave heating on the formation and depletion of molecules other than CH^+ has only been partially investigated. Shock fronts do cause instantaneous heating, but they affect the internal energy modes of molecules less strongly than the translation modes. Their net effect on chemical reaction dynamics is thus a complex nonequilibrium one. Gas phase models should include allowance for the accretion of atoms and molecules onto solid grains. This process may place an ultimate limit on the molecular complexity achievable by gas phase processes.

Gas phase models of dense interstellar clouds have successfully predicted abundances of several types of unusual molecules including free radicals (e.g., CCH), molecular ions (e.g., HCO^+), and metastable isomers (e.g., HNC). Another strength of these models is their prediction of isotopic fractionation via chemical reactions. Although the D/H ratio is $1\text{-}3\times10^{-5}$ throughout much of the universe, abundances of the deuterated forms of certain molecules can be enhanced far above this fractional abundance, especially in the cooler dense clouds. Indeed, ratios of DCO^+/HCO^+ and DNC/HNC near unity have been reported. Such enhancements are easily understood in terms of zero-point energy differences between hydrogen and deuterium bonds, which render particular directions of ion-molecule isotopic substitution reactions exothermic or endothermic, and hence rapid or slow. The principal reaction in deuterium enhancement is thought to be

$$H_3^+ + HD \rightarrow H_2D^+ + H_2$$

This reaction is exothermic by 0.02 eV in the left-to-right direction, and is much more rapid in this direction at interstellar temperatures. The ratio of the rate of the forward reaction to the rate of the backward reaction is a sensitive function of temperature. The ratio of HD to H_2 is thought to be twice the normal D/H abundance ratio. Because H_3^+ is a trace constituent of clouds and HD is abundant, the above reaction can transfer deuterium to H_2D^+ efficiently. The ion H_2D^+ can then react with other species to produce molecules with enhanced deuterium contents. For example, the reaction

$$H_2D^+ + CO \rightarrow DCO^+ H_2$$

produces DCO^+. More work is needed on the measurement of these and other possible critical reaction rates at low temperatures. Using a limited number of possible ion-molecule reactions, one can deduce certain parameters of the clouds from measured DCO^+/HCO^+ ratios. Specifically, one can deduce upper limits to the fractional electron abundance, the carbon monoxide abundance, and the kinetic temperature. This analysis indicates that the fractional electron abundance of dense interstellar coulds is at most 10^{-7}, which in turn implies that gas phase metallic element abundances are depleted severely from the cosmic values. (Otherwise the electron abundance would be 10^{-6}.)

Can gas phase processes produce the larger interstellar molecules observed? To produce these species, normal ion-molecule and ion-electron reaction sequences must involve a larger number of reactions. The probability that a crucial step in a chain of reactions involves an endothermic, unallowed process increases as the chain is lengthened. To date, no investigator has deduced sequences of normal ion-molecule reactions that would produce the larger species. It has recently been postulated, however, that certain radiative association processes involving a molecular ion and neutral molecule can be very efficient at low temperatures. If so, these reactions could aid in the production of larger species. Detailed theoretical treatments indeed seem to suggest that radiative association can reach 100% efficiency for certain molecular collision partners at temperatures below 100 K. An important laboratory verification of these theories has recently been accomplished. The reaction studied

$$CH_3^+ + HCN \rightarrow CH_3CNH^+ + h\nu$$

was found to be rapid at room temperature (one stabilized complex per 10 collisions), and to increase in efficiency as the temperature was reduced. Studies of more such reactions are needed, however, as is verification that the process is truly a radiative one. The identification of emitted photons would be most welcome. In addition, the theoretical treatments themselves can be improved. High priority should also be given to incorporating predicted radiative association rates into detailed cloud models, to determine whether or not they are sufficiently rapid to produce the observed larger interstellar molecules. Preliminary assessments show that calculated radiative association rates may be sufficiently rapid for this purpose.

Processes on the Surfaces of Grains

Detailed studies of grain processes are not as numerous as gas phase studies. Most semiquantitative models of *in situ* molecule formation on dust grains consider the latter to serve as passive bodies on which atoms and molecules can stick via "physical adsorption." Consider two hydrogen atoms that stick to a grain. The hydrogen atoms can migrate from one binding site to another, find one another, and stick together, with the chemical binding energy being transferred into the lattice modes of the dust particle. Hydrogen atoms can also coalesce with less mobile heavy atoms and molecules that are stuck on a grain surface, to produce hydrogen-rich heavier species. The newly formed molecules can evaporate into the gas phase if the adsorption energy is sufficiently low (e.g., H_2), but in the case of most heavy molecules, detachment from the grain remains a poorly understood process. Some suggested mechanisms for grain ejection include ejection during chemical reaction, photoejection, shock-wave-induced ejection, grain explosion, and grain heating caused by molecule formation. Upon release to the gas phase, molecules can be destroyed by gas phase processes or be readsorbed on grains. Activation energy barriers will exist for surface processes as well as for gas phase processes, unless the surface plays an active "catalytic" role. Thus, reactive processes on passive grains are normally also limited to atom-atom, atom-free radical, or free radical-free radical reactions. (Ions are thought to be unlikely adsorbates on grain surfaces.)

Despite the uncertainties associated with the various grain processes, estimates of the formation rates of molecules on passive grain surfaces have been made and models have been constructed. A model that included the larger interstellar species predicts that sufficient amounts of these species can be produced on grain surfaces to explain their observed abundances. However, this model excludes molecular

depletion via rapid gas phase processes: a model including this effect should be constructed.

Photochemical Processes in Icy Grain Mantles

If UV radiation penetrates dense clouds to a sufficient extent, the interesting possibility of photochemistry in grains emerges. Ultraviolet radiation can produce reactive radicals in the icy mantles of grains, and these in turn can combine into complex organic species. Grain "explosions" can return these species to the gas phase. Detailed studies of these processes are in progress in a laboratory simulating interstellar conditions. One of the interesting consequences of this work has been the production of a significant amount of highly complex, refractory, condensed organic material. It is possible that a substantial portion of the biogenic elements which ultimately were incorporated in the terrestrial planets (chapter VII) entered the solar system in this form, associated with inorganic interstellar grains.

It is perhaps tempting to conclude that, because molecular hydrogen can only be formed in clouds via grain surface processes, all species are probably formed on grain surfaces. One is quickly disabused of this notion, however, by the fact that grain models significantly underestimate the hydrogen deuteride (HD) abundance. The observed HD abundance can be accounted for only by the following sequence of gas phase reactions:

$$H + \text{cosmic ray} \rightarrow H^+ + \text{electron}$$

$$H^+ + D \rightarrow D^+ + H$$

$$D^+ + H_2 \rightarrow HD + H^+$$

Clearly, more research on the underlying physical and chemical processes occurring on grains is needed to resolve the question of the extent of their role in *in situ* molecular evolution.

UNSOLVED PROBLEMS AND RESEARCH OPPORTUNITIES

In this section a wide variety of important research topics are listed and discussed briefly. Most of these opportunities have already been noted in the body of the text.

Observational Studies

1. Large molecule identification: it is important for radio astronomers to determine how complex a chemistry has evolved in dense clouds. The tentative detection of glycine should be a boost to these studies.
2. Excitation condition studies: dense clouds are clearly not homogeneous in temperature. Observational studies of protostellar and shocked regions can shed light on the physical conditions, using molecules as probes. Particularly relevant here are submillimeter observations of transitions between excited rotational levels of molecules and near-IR observations of transitions between molecular vibrational levels.
3. High-resolution studies: observations are beginning to indicate large-scale clumping of interstellar gas clouds.
4. Transient molecule identification: the interstellar medium is an excellent source of gaseous transient molecules (free radicals and ions). As quantum chemical predictions of the rotational frequencies of transient species improve, it should be possible to search for these species directly in space. Such studies can benefit laboratory chemistry, because transient species are normally seen as laboratory intermediates and have poorly understood structures.
5. Infrared studies of clouds and circumstellar sources: radio astronomy (this term includes microwave, millimeter, and even submillimeter studies) is the basic technique for studying dense clouds. However, the rotational spectra of molecules cannot easily be seen for species without dipole moments. Infrared spectroscopy can be undertaken for such species, which include important hydrocarbons such as methane; and, via quadrupolar selection rules, symmetric molecules such as H_2. Thus, IR astronomy serves as a valuable complement to radio astronomy. Circumstellar and protostellar sources with continuum IR backgrounds can be studied by IR absorption spectroscopy. These sources are themselves of extreme interest. Infrared studies will probe the broad resonances attributable to solid grains, in addition to gaseous molecular transitions. Better wavelength resolution for this technique will be crucial in establishing the

spectral signatures of various mixtures and complex organic materials.

Experimental Studies

1. Gas phase spectroscopy: laboratory spectroscopy is the basis of all molecular astronomical studies. Of particular interest are studies on rotational transitions of transient species and those stable species with incompletely studied spectra, especially in the high-frequency (submillimeter) microwave region.

2. Grain spectra: some work has been undertaken in laboratory simulation of the IR, visible, and UV spectra caused by grains. More work of this type is needed to decipher a variety of spectral features recently seen by IR astronomers, as well as the classic diffuse bands in the visible wavelength range.

3. Ion-molecule reactions: gas phase models of clouds are based on laboratory studies of reaction rates. Some reactions are of particular importance; at the head of the list are radiative association processes leading to complex molecules. Almost equally important are the branching ratios of neutral products arising from recombination reactions between polyatomic ions and electrons.

4. Isotopic exchange processes: it is of great importance to measure rate processes that lead to isotopic fractionations at low temperatures.

Theoretical Studies

1. Quantum chemistry: quantum chemical calculations are urgently needed in several areas of interstellar chemistry. Calculations on the rotational frequencies of transient species difficult to produce in the laboratory can aid astronomers in finding these elusive species in space, and can aid spectroscopists in finding them in the laboratory. Calculations on likely processes undergone by molecules adsorbed on grain surfaces can aid in an explanation of grain chemistry and its role in the production of large species. Calculations of potential surfaces relating to important reactions that cannot be studied in the laboratory can be used in theoretical scattering calculations. Finally, calculations of radiative decay rates of excited molecules are needed as input for radiative association calculations.

2. Inelastic scattering: theoretical cross sections are needed for inelastic scattering processes that populate excited rotational states of molecules seen in emission so that the detected spectral lines can be analyzed to yield abundances.

3. Radiative association: theories of the rates of radiative association reactions need to be improved so that the role of this process in producing molecules can be better assessed.

4. *In situ* modeling: models of interstellar dense clouds must be extended to include inhomogeneous physical conditions, radiative association processes, grain formation rates, and other complexities such as gas clumping.

5. "External" source modeling: external chemical sources must be explored in more quantitative detail than has been done previously.

6. Grain physics: the physics of the various processes which can occur on and in grains has to be worked out in much more detail than has hitherto been the case. An exciting prospect is the further exploration of photochemical reactions, free-radical storage, and grain explosions.

7. Isotope ratios and their preservation: astrophysicists are beginning to understand how isotope fractionation occurs in interstellar clouds. What is also needed is an understanding about how such fractionations can be preserved under the conditions of gravitational collapse (chapter V) that lead to the formation of protostars and protostellar nebulae.

8. Cloud collapse: the detailed chemistry and physics of interstellar clouds during gravitational collapse must be investigated.

9. Data interpretation: theory can be used to help interpret observational data. An example is the use of ion-molecule reaction schemes to derive upper limits to cloud electron abundances, carbon monoxide abundances, and temperatures from measured DCO^+/HCO^+ ratios.

Additional Reading

Allen, M.; and Robinson, G. W.: Formation of Molecules on Small Interstellar Grains. Astrophys. J., vol. 195, 1975, pp. 81-90.

Green, S.: Interstellar Chemistry: Exotic Molecules in Space. Ann. Rev. Phys. Chem., vol. 32, 1981, pp. 103-138.

Greenberg, J. M.: Dust in Dense Clouds: One Stage in a Cycle. Submillimetre Wave Astronomy, J. P. Phillips and J. E. Beckman, eds., Cambridge Univ. Press, 1982, pp. 261-306.

Herbst, E.: A New Look at Radiative Association in Dense Interstellar Clouds. Astrophys. J., Pt. 1, vol. 237, 1980, pp. 462-470.

Herbst, E.: An Additional Uncertainty in Calculated Radiative Association Rates of Molecular Formation at Low Temperatures. Astrophys. J., Pt. 1, vol. 241, 1980, pp. 197-199.

Prasad, S. S.; and Huntress, W. T., Jr.: A Model for Gas Phase Chemistry in Interstellar Clouds: I. The Basic Model, Library of Chemical Reactions, and Chemistry Among C, N, and O compounds. Astrophys. J. Suppl. Series, vol. 43, 1980, pp. 1-35.

Scoville, N. Z.: Near Infrared Spectroscopy of Protostars. Phil. Trans. R. Soc. London, vol. A, no. 303, 1981, pp. 487-496.

Solomon, P. M.: Interstellar Molecules. Phys. Today, vol. 26, 1973, pp. 32-40. (Radio observations of dense clouds.)

Watson, W. D.: Interstellar Molecule Reactions. Rev. Mod. Phys., vol. 48, 1976, pp. 513-552. (Includes isotopic fractionation.)

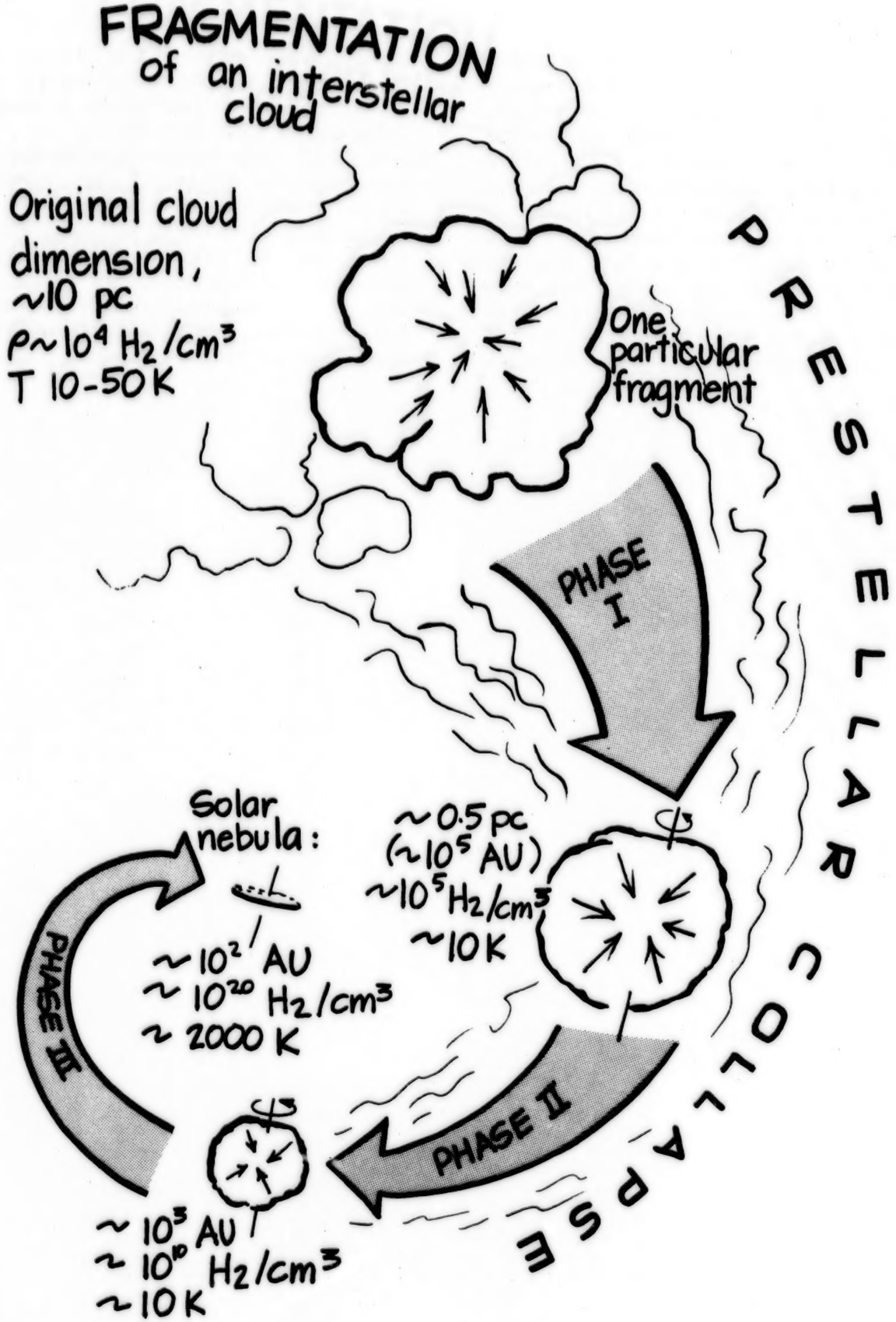
FRAGMENTATION
of an interstellar
cloud
Original cloud
dimension,
~10 pc
ρ~10⁴ H₂/cm³
T 10-50K
One
particular
fragment
PRESTELLAR COLLAPSE
PHASE I
~0.5 pc
(~10⁵ AU)
~10⁵ H₂/cm³
~10K
PHASE II
~10³ AU
~10¹⁰ H₂/cm³
~10K
PHASE III
Solar
nebula:
~10² AU
~10²⁰ H₂/cm³
~2000 K

Figure 4.

V

Protostellar Collapse

This chapter deals with the transition of matter from the low-density, large-scale cloudy structures discussed in the preceding chapter to the higher-density, smaller-scale structures of newly formed or forming stars and their associated nebulae of gas and dust. Subsequent chapters will treat processes in the nebula of one particular star, the Sun.

The protostellar collapse phase in the evolution of cosmic matter has proven to be difficult to study. Some of the obstacles to observational study have been (1) protostars are formed in clouds of gas and dust, and the dust permits only long-wavelength radiation to penetrate the clouds; (2) adequate instrumental sensitivity and resolution, both spatial and spectral, has been lacking in this wavelength range; and (3) this phase of evolution is short-lived (10^4–10^5 yr) by astronomical standards, thereby making it difficult to observe collapse in progress.

Some of the obstacles to theoretical progress have been (1) a lack of observational data to both guide and test theoretical models, and (2) the intrinsic complexity involved in a comprehensive calculation of the collapse of a protostar. This complexity has led theorists to carry out numerical experiments of gradually increasing sophistication in order to gain insight into the qualitative nature of protostellar collapse.

Although the final stages of cloud collapse, namely star formation and planetary accretion, are understood only vaguely from past observational and theoretical work, we can predict that enormous progress will be made in this particular area during the next 20 yr. The techniques of millimeter interferometry and IR spectroscopy, which have been under development in recent years, are about to provide the long-sought observational probes matched to the spatial scales (a few arcsecs) and physical conditions ($n(H_2)$ = 10^4–10^{14}/cm^3, T = 10–2000 K) expected in the collapse phase. We expect the interferometric data to reveal many details of the prestellar cloud fragmentation process; the IR spectroscopy will be used to study the gas dynamics along the collapse path, thus pinning down one of the most uncertain areas in the theoretical models.

This chapter is divided into five sections. A general descriptive overview of the collapse process and a listing of key questions relating that process to the evolution of the biogenic elements are given in the next section. More detailed discussions of our current observational and theoretical understanding of the three main phases of collapse are given in the following three sections. A summary of major unsolved problems relating to protostellar collapse and its role in the evolution of the biogenic elements, as well as a listing of promising near-term research opportunities addressing some of these problems, are given in the last section.

PROTOSTELLAR COLLAPSE AND THE BIOGENIC ELEMENTS: AN OVERVIEW

Protostellar Collapse

A comprehensive discussion of protostellar collapse is beyond the scope of this document;

interested readers are referred to review papers in the list of suggested reading at the end of this chapter. Here we provide only a brief descriptive overview of collapse, focusing on those aspects of it that pertain to the evolution of the biogenic elements.

It is usually assumed that the starting point for protostellar collapse is a dense cloud of the type discussed in the previous chapter. As depicted schematically in figure 4, either the cloud is in equilibrium, and breaks up into smaller stellar-mass systems, each of which begins to collapse; or the original large cloud is itself undergoing collapse, and fragmentation occurs during collapse of the parent cloud. By one means or the other, nature somehow finds a way to separate stellar-mass blobs from the much more massive interstellar clouds. The details of this fragmentation process are not understood; it is not even known at what stage or stages in the collapse the fragmentation occurs. In this document we will simply suppose that fragmentation has occurred, and that we can concentrate on a single protostellar cloud fragment.

Even if we can bypass the issue of fragmentation, we are still faced with a very difficult problem. A wide variety of physical phenomena must be considered in any comprehensive calculation of protostellar collapse. For example, it is well documented that there is a general background magnetic field in the Galaxy, a field with a strength of a few microgauss. While this field strength is small by terrestrial standards, it is sufficient to be a significant (in some cases a dominant) force in determining the structure and evolution of interstellar clouds. In addition to magnetic fields, there is also rotational motion to consider. Again, the rate of rotation is actually very small ($\gtrsim 10^{-14}$ rad/sec), so small that some of the interstellar clouds may not even complete one full revolution during their lifetime. However, the critical quantity is not the rate of rotation, but rather the angular momentum resulting from that rotation. The specific angular momentum of a typical interstellar cloud is some five to six orders of magnitude greater than that of the most rapidly rotating main-sequence star. Clearly, nature has found a way to remove most of the angular momentum from a collapsing protostar. More will be said about this point below.

The wide variety of physical phenomena involved in protostellar collapse (hereafter referred to simply as collapse) makes it necessary to use numerical experiments to study the problem in its fullest complexity. The types of numerical experiments conducted to date appear in table 3. While many important questions concerning collapse remain, significant progress has been achieved. In particular, one can provide a qualitative description of a collapse.

It is most convenient to describe collapse in terms of evolution in density and temperature, as these are variables important to the question of the evolution of biogenic elements. Shown in figure 5 is the evolution of the interior (i.e., central) temperature and density during the collapse of two protostars, one of about 40 solar masses and one of about 1 solar mass. One can divide the evolution depicted in figure 5 into three distinct phases: Phase I, in which the temperature decreases with increasing density; Phase II, in which the temperature is approximately constant during collapse; and Phase III, in which the temperature increases with increasing density. There are many important differences between the physical processes occurring during these three phases, which is why we have chosen to use them as a framework for the remainder of the discussion.

In order to evaluate the observability of objects in the three phases of collapse, we have listed in table 4 the physical conditions (density and temperature) experienced during each phase. The temperatures given are those predicted from calculations which consider only the energy release from gravitational collapse. These temperature estimates may therefore be viewed as lower limits to the temperatures in sources that will be observed, because often there will be significant additional radiative heating from adjacent stars which formed earlier, or from localized shock fronts. In table 4 we also give the linear and angular diameters (assuming a distance of 500 pc) of condensations with total mass ~50 $M_{\odot}$, and the typical velocities expected on the basis of the virial theorem.

The two principal approaches to observations of star formation regions (millimeter wavelength spectroscopy of the pure rotational transition of molecules, and IR continuum measurements of the dust emission) have yielded spectacular discoveries relating to Phase I and late Phase III,

TABLE 3.– PHYSICS INCLUDED IN PROTOSTELLAR COLLAPSE CALCULATIONS

Physical input	Type (symmetry) of model		
	Spherical (one-dimensional)	Axial, equatorial (two-dimensional)	Equatorial (three-dimensional)
Hydrodynamics and self-gravitation?	Yes	Yes	Yes
Equation of state and thermodynamics?	Complete	Complete	Isothermal or adiabatic ideal gas
Radiative energy transport: diffusion approximation?	Yes	Yes	No
Radiative energy transport: frequency dependent?	Yes	Limited	No
Convective transport?	Yes	No	No
Simple viscosity?	No	Yes	No
Molecular chemistry?	Yes	Limited	No
Magnetic field?	Not applicable	Yes	Limited
Gas-dust interaction?	Yes	Yes	No

but few if any objects have been studied so far that we can clearly identify with Phase II. The reason for this observational insensitivity at Phase II is easily seen in table 4. The single telescopes employed at millimeter wavelengths all have resolution $\gtrsim$30 sec of arc, and the transitions observed are moderate or low in excitation requirements. They are therefore not very specific to the relatively high densities of Phase II. On the other hand the IR photometry at $\lambda < 100$ μm requires the presence of grains at temperatures $\gtrsim$30 K for significant emission; when this is the case, one is generally observing the luminosity of either an embedded star, or at best the late Phase III contraction. As discussed below, we expect that in the coming years significant progress can be achieved in the observation of objects in the intermediate Phase II.

Questions Concerning the Processing of Biogenic Elements

Generally speaking, there are three ways in which biogenic elements can be processed: they can be created, they can be destroyed, or their state can be altered. Elements are not created or destroyed to any significant extent during protostellar collapse, but their states can be altered. Here we are using "alteration of state" in a very broad sense, to include, for example, chemical reactions that move the biogenic elements from one molecule to another, or the entrapment of a biogenic element on the surface of a dust grain. With this in mind, one can pose three first-order questions concerning the processing of biogenic elements during protostellar collapse:

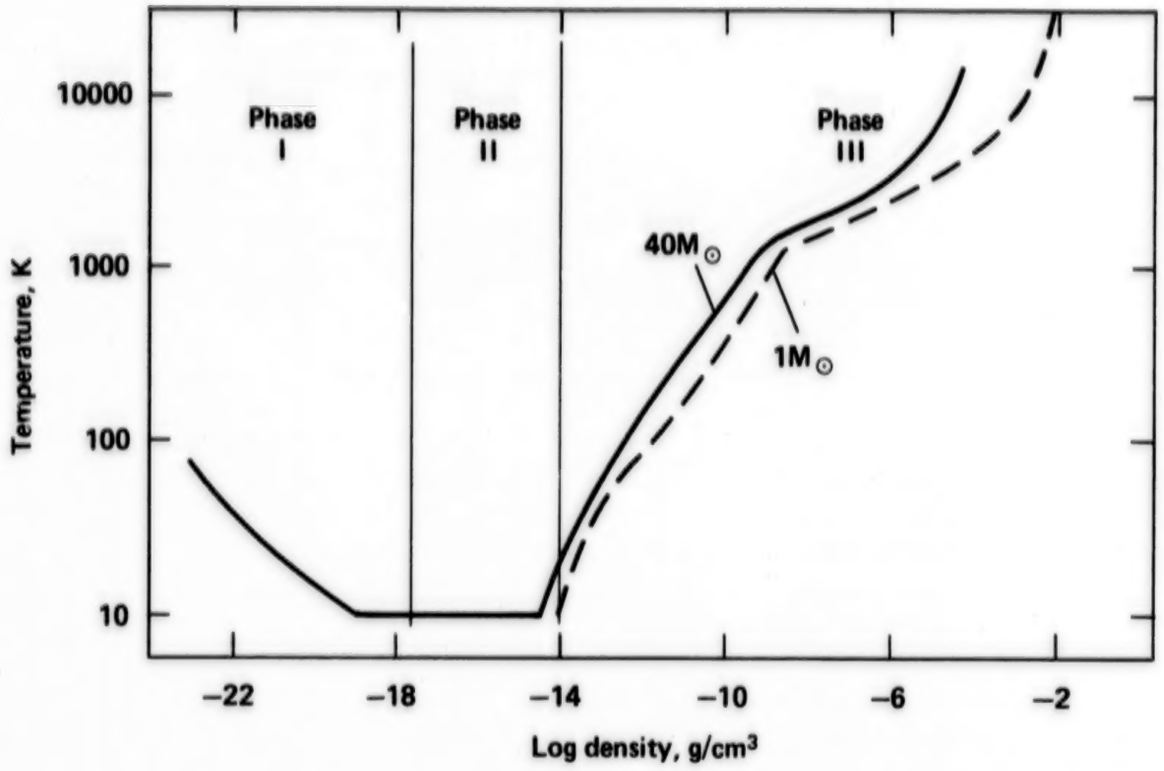

Figure 5.– Evolution of central temperatures and densities during the collapse of 1 $M_\odot$ and 40 $M_\odot$ protostellar clouds. Reprinted courtesy of P. Bodenheimer and *The Astrophysical Journal*, published by the University of Chicago Press; ©1978 The American Astronomical Society.

TABLE 4.– THREE PHASES OF PROTOSTELLAR EVOLUTION

Phase	Temperature, K	Density $n(H_2)/cm^3$	Diameter[a]	Angular diameter,[b] arcsec	Velocity,[c] km/sec
I	10	10^4–10^5	0.7–0.3 pc	300–140	1
II	10	10^5–10^{10}	10^5–10^3 AU	140–3	1–8
III	10–2000	10^{10}–10^{20}	$<10^3$ AU	<3	8

[a]For a ~50-$M_\odot$ cloud fragment.
[b]For a ~50-$M_\odot$ cloud fragment, at a distance of 500 pc.
[c]Estimate of velocity from the virial theorem.

1. How are the elemental and isotopic compositions of the gas phase altered?
2. How are the elemental and isotopic compositions of the dust grains altered?
3. How are biogenic elements transferred between the gas phase and the dust grains?

The answers to these questions will depend on the phase of collapse, as well as on a variety of second-order questions concerning collapse:

1. What is the ionization state of the protostar?
2. What is the thermodynamic state of the protostar: in particular, is it in equilibrium?
3. Is the protostar spatially homogeneous, and is it a closed system?

In the following three sections, we follow a collapse through the three phases that we have identified, and outline what is known both observationally and theoretically concerning these questions.

PROTOSTELLAR COLLAPSE: PHASE I

Phase I of collapse occurs at low densities, i.e., $\lesssim 10^4$-10^5 H_2 molecules/cm^3, and is characterized by decreasing temperature as the density increases. This is a consequence of more efficient cooling at the higher densities. The dynamical state of Phase I is rather quiet, large collapse velocities having not yet been generated.

Observational Evidence

Over the last decade, a host of millimeter-wavelength molecular transitions have been detected in molecular clouds: nearly all of these are well suited to probing the physical conditions and chemistry during Phase I. For most of the rotational transitions, radiative decay rates and collision cross sections are such that the level populations thermalize at densities above 10^5/cm^3. Thus maps of the CS, HCN, and H_2CO lines have been used to delineate the density structures in clouds up to $n(H_2) \sim 10^5$/cm^3. For this same regime, the CO line provides an excellent probe of the kinetic temperature, because its extremely slow radiative decay ensures that the level populations are thermalized at $n(H_2) \geqslant 10^3$/cm^3. The CO observations can therefore distinguish those high-density fragments where stars have already formed (here the CO line will indicate >10 K temperatures) from those fragments truly in Phase I *prestellar* collapse.

The well-studied core region in the Orion molecular cloud is undoubtedly of the former variety. The great number of high-excitation molecular transitions seen there indicates that the density in the central 30 sec of arc (a region $\sim 2\times10^{17}$ cm in extent) approaches 10^6/cm^3. At the same time it is clear that star formation has already commenced: at least two self-luminous sources (BN and IRC-2) are detected by near-IR photometry, each with luminosity $>10^4$ $L_\odot$ and color temperatures $\gtrsim$300 K. The temperature estimated from the CO lines rises to ~80 K in this region. Notwithstanding the clear evidence that some star formation has already occurred here, it still may be worthwhile to view the gas density structure here in the context of Phase I and Phase II evolutionary models; the density structure over the inner few arcminutes of Orion may still retain traces of these earlier configurations for some time after the first stars have formed. Making the gross simplification of spherical symmetry, the best fit to both the millimeter-line and submillimeter continuum data is provided by an $r^{-1.5}$ density law, in reasonable agreement with theoretical predictions.

Inasmuch as the Orion cloud shows evidence of star formation at several sites, probably all within the last 5×10^5 yr, these data also furnish important constraints on the stage at which two distinct scales of fragmentation occur during collapse. Within the central 15 arcmin (~2 pc), at least three separate centers of activity are seen (the Trapezium, the BN-KL IR sources, and the OMC-2 sources). The former are separated by ~0.2 pc, the latter by ~1.7 pc. In each area it is clear that stars have formed within ~0.05 pc or less of one another. This demonstrates that fragmentation takes place first on large scales, then on the smaller scale of individual stellar masses.

Regions undergoing Phase I collapse, but with no stars yet formed, are somewhat harder to observe than the situation just described, owing to their lower temperatures. Probably the most interesting such region is the nearby dark cloud known as B5, a cloud that exhibits central symmetry in the density structure and no evidence

of central heating. Lower temperatures are inferred for the cloud center than for the outer layers, in agreement with the theoretical predictions, but this could also be due to increased UV heating in the cloud boundary layer. Most spectacular perhaps is recent kinematic data suggesting that rotation in the cloud interior may be braked, possibly by magnetic torques. It is of paramount importance that direct measurements of these magnetic fields be made.

Observations provide fragmentary evidence of chemical fractionation in clouds. $^{13}CO/H$ is seen to decrease by a factor of ~2 with increasing cloud density. Heterogeneity of chemical abundances is also clear in other species. For example, the HCO^+ distribution in the Orion cloud is very different from that of CO, CS, or HCN, but the correlation with density structures is not well established. Observational studies to analyze these abundance variations relative to variations in the physical conditions from point to point would be especially useful.

Theory

It is likely that magnetic fields, if present, will remain trapped in the collapsing protostar throughout Phase I, even if one allows for the possibility of ambipolar diffusion. (Ambipolar diffusion is the process whereby a magnetic field and the charged particles which are tied to the field move relative to the un-ionized material that constitutes the bulk of the mass of a protostar. The neutral particles and the magnetic field are coupled via collisions between the neutral and charged particles.) In fact the strength of the magnetic field will be amplified during the collapse, scaling approximately as the square root of the neutral gas density. Thus one expects to find reasonably large magnetic fields in this phase of collapse evolution. Calculations of the degree of ionization of protostellar gas indicate that the fractional ionization (the ratio of the ion to neutral number densities) will vary as the inverse square root of the neutral density. As noted in the previous chapter, the degree of ionization can be important in certain chemical reactions.

There is no theoretical evidence to suggest that there will be significant fractionation between gas and dust in this phase of collapse. The dust grains will be tied to any magnetic fields that are present in the protostar, but as noted above, the magnetic field is trapped in the collapsing material. Also, at this stage of collapse, the dust grains are small and are well coupled to the gas, so they tend to follow the motion of the gas.

In contrast to the apparently constant gas/dust ratio, there is now good theoretical evidence that significant fractionation of both elemental and isotopic ratios will occur during Phase I evolution. Recent numerical studies have shown that the interior regions of Bok globules, small dense clouds, and perhaps also somewhat more massive clouds are characterized by a lower $^{13}CO/H_2$ ratio than is representative of lower-density clouds. The $^{13}CO/H_2$ ratio that is usually found in clouds is $\sim 10^{-6}$, but the numerical work indicates that this ratio may be as low as $3\text{–}4 \times 10^{-8}$ at densities near those that mark the transition from Phase I to Phase II. The decrease in this ratio begins at a density of $\sim 10^3/cm^3$.

Finally, we note that there is some theoretical evidence indicating significant mixing of material from outside a collapsing protostar with the protostellar material. This external material is both general background material from the parent cloud of the protostar and debris from other stars that already may have formed in the parent cloud. Recent discoveries of isotopic anomalies in meteorites have led to much speculation that the collapse of the protostar which ultimately formed the Sun and its planetary system was triggered by a shock wave from a nearby supernova. While this possibility cannot be ruled out, there is no theoretical reason to suppose that such events generally play a major role in the initiation of collapse.

PROTOSTELLAR COLLAPSE: PHASE II

Phase II starts at a density of about $10^5/cm^3$, and ends when the density has increased to a value of $\sim 10^{10}/cm^3$. The density at the end of Phase II is dependent on the mass of the protostar, but only weakly (see fig. 5). Operationally, the end of Phase II occurs when the protostar becomes optically thick to the radiation arising

from the generation of compressional energy during collapse. The major characteristic of Phase II is that the temperature remains nearly constant during collapse, at a value of ~10 K. Unlike Phase I, Phase II is highly dynamic. As a consequence, relatively less time is spent in this phase of collapse than is spent in Phase I, even though Phase II is more extensive in terms of the range in density involved. Its combination of (1) low temperature, (2) high density (i.e., small size), and (3) short time scale make this phase of collapse very difficult to study observationally.

Observational Evidence

At present the phase of collapse least accessible to observations is Phase II. As pointed out above, this is due both to inadequate spatial resolution in the millimeter-line observations and to the lack of transitions at millimeter wavelengths specifically sensitive to densities in the range 10^8-10^{10}/cm^3 and low temperatures. We expect that this deficiency will be made up in the next few years by the new millimeter-wavelength interferometers and by spectroscopy in the far IR from high-altitude telescopes (e.g., the NASA Infrared Telescope Facility). The interferometers (operating at $\lambda \sim 1$ mm) may be especially powerful in mapping out the distribution of dust continuum radiation at resolutions of a few seconds of arc. As the dust is optically thin at long wavelengths, these data will provide a clear picture of the spatial distribution of dust, and presumably also of the gas, during condensation. Such observations have the additional advantage that they will not be restricted to sources in which stars have already formed, since the radiation emitted at $\lambda = 1$ mm is not very dependent on the presence of high-temperature dust. In the long run probably the best prospect for observing Phase II is offered by the proposed NASA Large Deployable Reflector (LDR) telescope. This telescope, to be deployed from the Space Shuttle, would provide ~1-arcsec resolution at $\lambda = 100$ μm.

Theory

The dynamical aspects of Phase II evolution are much different than those of Phase I. For example, whereas magnetic fields may play a dominant role in the dynamics of Phase I, they cease to be of any significance dynamically by the mid to late stages of Phase II. However, recent numerical studies indicate that the strength of the magnetic field continues to be amplified during collapse. That is, although the magnetic fields are not dynamically significant, they are unable to diffuse out of the collapsing protostar. It is during Phase II that the dynamical effects of rotation are likely to be most evident. During Phase I, the rate of rotation is probably maintained at a fairly constant value because of magnetic breaking. Once the magnetic fields are no longer dominant, collapse proceeds at constant angular momentum rather than at constant angular velocity.

The buildup in rotational forces that occurs as the collapsing protostar spins up has been shown to lead to fragmentation of the protostar if the rate of rotation is relatively high. The details of this fragmentation depend on many parameters, but the fragmentation usually involves the formation of a ring-like structure in the central regions of the protostar. Such a structure is highly unstable to further breakup into a small number (about two to four) of blobs orbiting the center of mass of the original protostar. The end result of this process is likely to be the formation of a binary system, with two of the ring blobs surviving. This picture is satisfying, because nature prefers to make binary systems; the number of single stars is a small fraction (<30%) of the total number of stellar systems. Finally, it should be noted that Phase II evolution is highly nonhomologous: the inner regions of the protostar evolve on much shorter time scales than do the outer regions.

Not much is known about the biogenic elements specifically. The variables such as temperature and pressure are fairly well specified during Phase II, but the details of chemical interactions either in the gas phase or between gas and dust are not. Also, very little is known about how the dust grains evolve during this phase. There is theoretical evidence to suggest that the degree of ionization at these higher densities decreases linearly with gas density. This behavior sets in at a gas density of ~10^9/cm^3, where recombination on dust grains becomes significant.

PROTOSTELLAR COLLAPSE: PHASE III

The transition to Phase III occurs when the temperature of the protostellar material begins to increase with increasing density. This occurs because the protostar becomes opaque to its own radiation. The evolution in Phase III is thus more nearly adiabatic. Because of the buildup of temperature with increasing density, there is a dramatic increase in the effects of gas pressure on the dynamics. This increase quickly reaches the point where gas pressure is able to halt the collapse, leading to the formation of an equilibrium core in the center of the protostar. (If fragmentation occurred in Phase II because of rotational effects, our comments on Phase III pertain to one of the binary protostars and not to the original protostar.) This core, which may be very small if the residual rotation is large, serves as an accretion center for the material remaining in the outer regions of the protostar. This accretion process ultimately leads to the formation of a nebula of the type discussed in the following chapter.

Observational Evidence

Because of its extremely small size and high density, a protostar evolving through Phase III can be studied only via IR spectroscopy at $\lambda \sim 2$-20 μm. These techniques have so far been applied only to the brightest of the embedded IR sources (e.g., the BN star in Orion), but as sensitivity improves for wavelengths longer than 5 μm, many more objects (presumably earlier in their evolution) will become accessible.

Observations made to date of BN serve to underscore the potential of this approach. Spectroscopic studies of BN made through the terrestrial windows at $\lambda = 2$-5 μm have yielded detections of over 100 separate transitions of HII, H_2, CO, ^{13}CO, $C^{18}O$, and atomic Na and Fe. The data serve to define the characteristics of the central star (e.g., the UV production rate and stellar dynamics) and the circumstellar nebulae at radial distances of 1-20 AU (both an HII region and a high-temperature neutral region are detected). In the circumstellar nebula, the CO lines show evidence of continuing accretion, despite the fact that the central star may have reached the main sequence.

In addition to serving as a probe of Phase III, which is not accessible otherwise, near-IR spectroscopy is also capable of detecting several important molecular species that have no radio-frequency transitions. Several molecules which are particularly abundant in solar nebula models (e.g., CH_4) can be detected only in the near-IR.

Theory

As indicated above, Phase III is less dynamic than is Phase II; however, it is considerably more complex in terms of its thermodynamics. The nearly adiabatic increase in temperature that occurs at the onset of Phase III continues until the temperature reaches a value of ~1800–2000 K, at which point the molecular hydrogen present in the cloud begins to dissociate. Once dissociation sets in, it serves as a sink for additional energy generated during further compression. Until most of the hydrogen is dissociated, there will be relatively little increase in the temperature of the gas. Once the gas does begin to heat again, it will encounter an ionization barrier which acts in a manner analogous to the dissociation barrier.

One of the more important parameters that determines the evolution of a protostar during Phase III, and thereby the processing of the biogenic elements during this phase, is the angular momentum of the protostar. If its specific angular momentum is low (i.e., comparable to the specific orbital angular momentum of Jupiter), then most of the collapsing protostar will reach fairly high density and temperature. If the specific angular momentum is higher, it is possible that a large fraction of the protostellar material will not reach high temperatures and densities.

An important issue is whether the temperatures reached during Phase III are high enough to vaporize the dust grains that are present in the collapsing protostar. As the outer regions of the protostar are accreted onto the inner equilibrium structure, be it a stellar core or an embryonic solar nebula, the energy associated with the in-fall must be dissipated in a shock and reradiated into the surrounding material. Very little quantitative information is available on this point. Even if the grains are not all vaporized (and there is experimental evidence that in the solar nebula they were not; chapter VII), their

composition and structure would almost certainly be altered during Phase III.

Finally, there is the issue of whether the protostar is homogeneous with regard to the spatial distribution of the biogenic elements during Phase III. As noted above, the collapse is very nonhomologous, and this gives rise to the possibility that there will exist significant spatial inhomogeneities in the distribution of both dust and gas. There is also good theoretical evidence that significant gas/dust fractionation will occur during Phase III.

UNSOLVED PROBLEMS AND RESEARCH OPPORTUNITIES

In this section we summarize some of the major unsolved problems concerning the processing of the biogenic elements during protostellar collapse, and identify what appear to be particularly promising near-term research opportunities in this area.

Observational Studies

From our discussion, one can see several directions in which future observations should proceed.

1. Much more can be done using existing millimeter-wavelength radio telescopes to systematically analyze the temperature, density, kinematics, and chemical fractionation in protostellar fragments during Phase I. Clearly more effort should be devoted to the analysis of regions without near-IR sources, because these sources may often confuse the interpretation of the observed structures.

2. The new millimeter interferometers show great promise for the study of late Phase I and early Phase II collapse. These instruments will be sensitive at angular scales down to ~10 arcsec in cold regions, and ~2 arcsec in centrally heated regions.

3. Later phases of the collapse and the subsequent dispersal of protostellar nebulae are best studied by IR spectroscopy. Far-IR spectroscopy ($\lambda \sim 100\ \mu m$) from above the terrestrial atmosphere, employing the rotational transitions of small molecules, is most appropriate for observing systems with intermediate densities and low temperatures. Spectroscopy at the shorter wavelengths corresponding to molecular vibrational transitions is the most powerful tool for observing the inner zone of circumstellar nebulae (radial distances of 1-50 AU). A very large improvement in sensitivity for near-IR spectroscopy is foreseen, with the advent of low-background spectrometers using array detectors.

Theoretical Studies

Several problems remain to be solved before a firm theoretical picture of protostellar collapse and its effect on the biogenic elements can be drawn. Perhaps the major one is understanding how and at what stages fragmentation occurs. Input from observations will be extremely helpful in addressing this problem. The major relevance of fragmentation to the issue of the biogenic elements is that the extent of homogeneity in spatial distribution of the biogenic elements, and also the extent to which biogenic elements from various volumes of gas external to a protostar mix with it. These factors could be very dependent on the details of the fragmentation process. Another important problem relating to the dynamics of collapse is the combined interaction of magnetic fields and rotation. As noted earlier, nature has found a way to remove most of the angular momentum from a protostar. It is currently thought that angular momentum is transferred out of a rotating cloud via Alfvén waves. To date this conjecture has not been shown to work in detail, but it appears very promising. A final problem having to do with the dynamics of collapse involves the role of turbulence. While there is good evidence that the parent clouds for a collapsing protostar have large-scale chaotic internal motion, there is no evidence that this chaotic motion is anything like laboratory turbulence, and there is no reason to suppose that classic isotropic turbulence should be present in these clouds. However, at some stage in collapse, it is likely that turbulence-like motion does occur, and this motion may affect the dynamics of the protostar as well as mix its various regions.

In addition to these dynamical problems, there are also problems concerning the alteration of the state of the biogenic elements. A great deal of work remains to be done on

low-temperature chemistry of all kinds. Particularly important is the determination of any elemental or isotopic tracers of the physical and chemical history of the biogenic elements during collapse. Given the wide variety of ways in which the elemental ratios of the biogenic elements can be altered, it is likely that the best tracers will be the isotopic structure of the biogenic elements. One of the more difficult and important problems involving the processing of the biogenic elements during collapse concerns the evolution of the dust grains in a protostar. How do their composition and size change, what role do they play in the chemistry of the gas, and how and when is there fractionation (separation) between the gas and dust?

The problems discussed above are difficult, but there are prospects for progress toward partial solutions of several of them. Numerical experiments, guided by observations, should soon provide insight on the problem of fragmentation. These experiments will also provide an answer to the question of whether magnetic fields can remove the necessary amount of angular momentum from a collapsing protostar, and will provide more realistic input models for calculations of the evolution of the solar nebula. Use of multifluid numerical schemes should also bring advances in understanding the evolution of dust during collapse, from the standpoint of chemical and physical evolution of the dust. Finally, the availability of large computers will make it possible and simpler to include self-consistent calculations of the chemical evolution of the biogenic elements during collaps.

Additional Reading

Bodenheimer, P.: The effects of Rotation During Star Formation. Fundamental Problems in the Theory of Stellar Evolution, Proceedings of the Symposium, Kyoto, Japan, July 22-25, 1980 (I.A.U. Symp. 93), D. Sugimoto, D. Q. Lamb, and D. N. Schramm, eds., D. Reidel (Dordrecht), 1981, pp. 5-26.

Bodenheimer, P.; and Black, D. C.: Numerical Calculations of Protostellar Hydrodynamic Collapse. Protostars and Planets: Studies of Star Formation and of the Origin of the Solar System. T. Gehrels and M. S. Matthews, eds., Univ. Arizona Press, 1978, pp. 288-322.

Werner, M. W.: Infrared Studies of Star Formation in Orion. Henry Draper Memorial Symposium on the Orion Nebula, A. E. Glassgold and P. J. Huggins, eds., Ann. N.Y. Acad. Sci., 1982, pp. 79-99.

Wynn-Williams, C. G.: The Search for Infrared Protostars. Ann. Rev. Astron. Astrophys., vol. 20, 1982, pp. 587-618.

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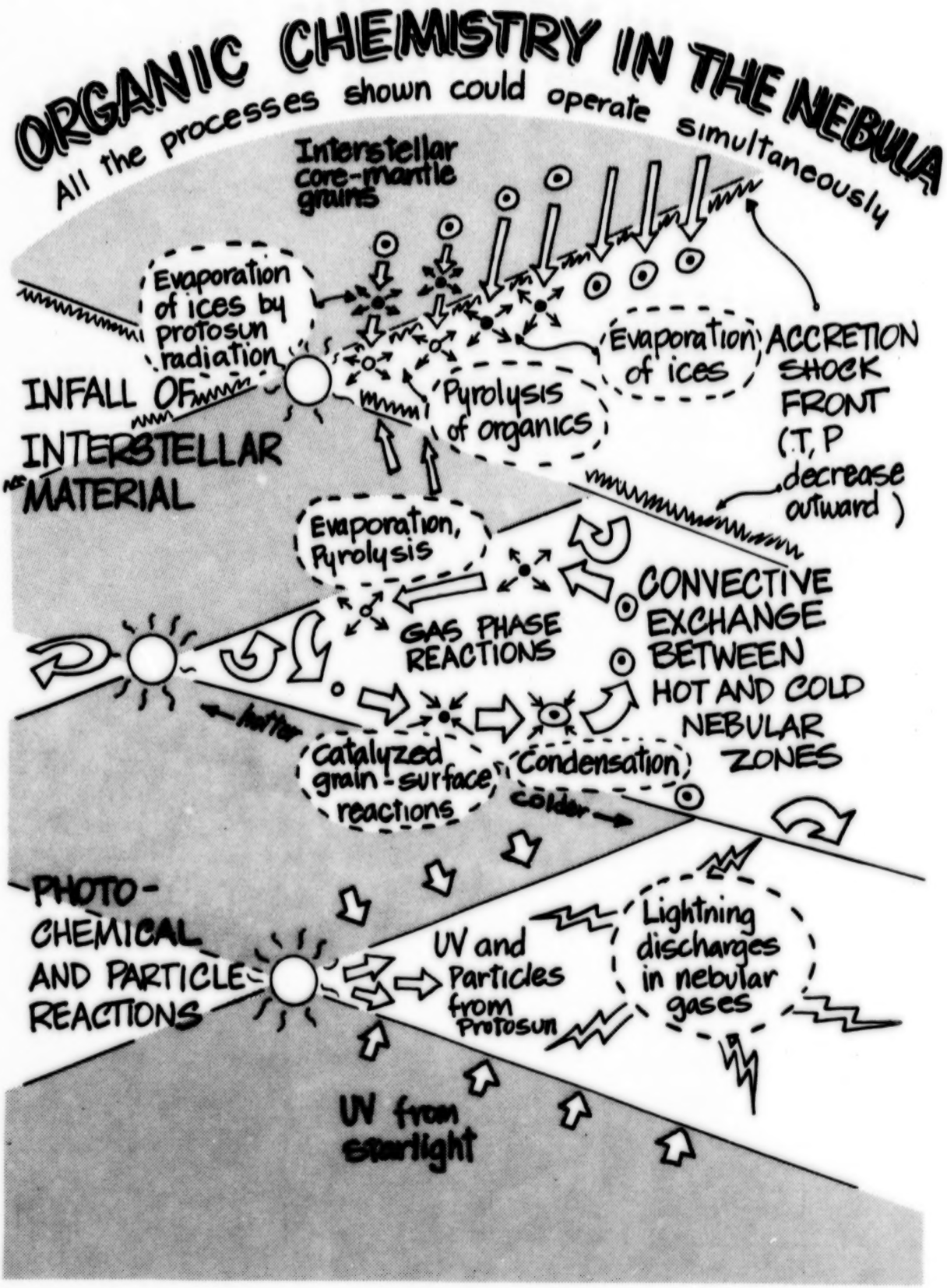

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VI

Chemical Evolution in the Solar Nebula

The previous chapters have treated astrophysical and star-forming processes in the galaxy at large. As we have seen, star formation also produces transient protostellar nebulae. In the remainder of this report we will focus on one particular star, our Sun, and its nebula. In the first section of this chapter we consider the processes that may have shaped the history of the biogenic elements and their compounds during their sojourn as gases and grains in the solar nebula (fig. 6). The second section deals with the natural samples that may bear evidence of this history.

In the preceding chapter, it was pointed out that major uncertainties exist concerning the total mass and angular momentum of the solar nebula formed during the final stages of protostellar collapse. Until these uncertainties are reduced or resolved, detailed models describing the thermal history of the solar nebula may be of limited value as a framework for interpreting the chemical evolution of the biogenic elements and compounds in the solar nebula. Nonetheless, there are some basic properties of the solar nebula that must be common to all models.

The elemental composition of the protostellar cloud which collapsed to form the solar system is not known a priori, but the solar nebula resulting from it is inferred to have had the same bulk composition as the Sun. Theoretical models of accretion disks indicate that protostellar collapse probably proceeded in a nonhomologous fashion. Infall heterogeneities and dynamical instabilities developed within the disk may have inhibited attainment of axial symmetry in its mass distribution. Moreover, abundant evidence from the study of meteorites (see below) lends credence to the view that certain isotopic and chemical heterogeneities, either inherited from the protostellar cloud or developed during collapse (or both), existed in the solar nebula from which the components of these objects accreted.

The nebular gases are expected to have been turbulent as a result of shearing in the differentially rotating nebula and also because of the disturbance associated with continuing in-fall of interstellar matter. Although the scale, intensity, and duration of these turbulent motions are model-dependent, they appear to be an inevitable property of protostellar nebulae. As such, turbulence provides an intrinsic mechanism for mass transport of dust and gas between and within different regions of the nebula. In theory, during the infall and subsequent nebular evolution, grains are expected to aggregate and settle to form a dust layer at the midplane of the rotating disk. Superimposed on this tendency would have been the perturbations created by convection.

The uncertainty in specific angular momentum (J/M) of the interstellar material that gave rise to the solar system, alluded to above and in chapter V, has a major effect on the properties of the nebula. If J/M for the solar system had a value typical for interstellar material, this appears to result in a structure with a large disk/protosun mass ratio which is gravitationally unstable, such that the nebular disk is expected to fragment into a set of giant gaseous protoplanets. If the interstellar material that gave rise to the Sun had atypically low J/M (<0.1 of the typical value), a smaller disk/protosun mass ratio results, and the nebula remains gravitationally stable. It is possible that "typical" interstellar J/M should not be assumed for the material antecedent to the solar system, since the Sun

is not a typical star. Most stars of the Sun's spectral class are members of binary or multiple star systems, which have much larger J/M than the solar system.

Interstellar gas and dust are thought to have continued to fall into the protosun and nebula at nearly the free-fall velocity, for $\sim 10^6$ yr after initial formation of the protosun. The gas was abruptly decelerated and compressed when it encountered a standing shock front that bounded the protosun and nebula. There its kinetic energy was converted to heat, most of which was radiated away. The gas experienced a transient heating at this time which, at small radial distances from the protosun, would have been severe enough to pyrolize complex molecules.

Infalling interstellar grains would have had a more complex thermal history. Approaching the protosolar system, they would have been irradiated by UV photons from the protosun, and (as they drew nearer) warmed by it. These influences would have tended to convert icy mantles on the in-falling dust grains into complex, nonvolatile organic substances, as discussed in chapter IV. When the grains encountered the nebula, they would not be decelerated at the shock front; they would penetrate the decelerated gas at high relative velocity, and would be gradually decelerated (and heated) by aerodynamic drag. The grains would have been drag-heated to substantially higher temperatures than the temperatures attained by the accompanying gases as a result of shock-heating. In the inner nebula, organic compounds in or on the grains would have been severely pyrolized; but at large radial distances, where infall velocities were lower, they could have survived entry into the nebula.

The infall of interstellar matter onto the protostellar core and its nebula, and also viscous dissipation of energy in the differentially rotating nebula, would have produced a gradient in temperature and pressure with values higher at the core and diminishing with increasing distance in the radial direction. This T,P distribution is expected to have changed as the protostar and its nebula evolved, but the rates of change and the maximum values for these parameters at various points in the nebula are poorly constrained by both theory and observations. At the end of the infall stage, the nebula's temperature, pressure, density, and thickness would have decreased with time as momentum transfer in the disk fed some of its substance into the protosun and spun the rest out to greater and greater distances.

From among the exploratory calculations carried out for a solar nebula, an example of a possible thermal evolution in the formation regions of the planets is shown in figure 7. Typical isobars during the warmest phase of this nebula model are plotted in figure 8. While it is unlikely that these calculations have mimicked the thermal evolution of the nebula, they serve to illustrate qualitatively some of the important changes to be expected in the thermodynamic conditions in the nebula over time and space. The particular nebula model characterized by figures 7 and 8 is expected to be gravitationally unstable, and would break into giant gaseous protoplanets.

Although we will not address specifically the fate of gases and grains in hypothetical giant gaseous protoplanets, these too are expected to have been endowed with convective motions, and with temperatures, pressures, and compositional gradients that changed with time. Therefore, many of the processes described below also could have occurred within them, but probably on different time scales than in the solar nebula. In theory, if the protoplanets lost their gaseous envelopes (by tidal stripping) before condensates in them had completely rained out onto their hot cores, the remaining grains and accreted planetesimals (which would have had widely different thermal histories) could have been released into the interplanetary medium and subsequently incorporated in other bodies.

Clearly, the presence of nebular gas had a major influence on the nature and duration of the physical and chemical processes operating on the biogenic elements and their compounds. But the period from the onset of collapse until the dissipation of the nebula remains uncertain, with possible time scales ranging from 10^4 to more than 10^6 yr.

Against this background of uncertainty we will consider first the processes operating on gases and grains that may have influenced the biogenic elements and their compounds in the solar nebula. For this purpose we assume that with the exceptions of H_2, and perhaps N_2, CH_4, and CO, the biogenic elements participated

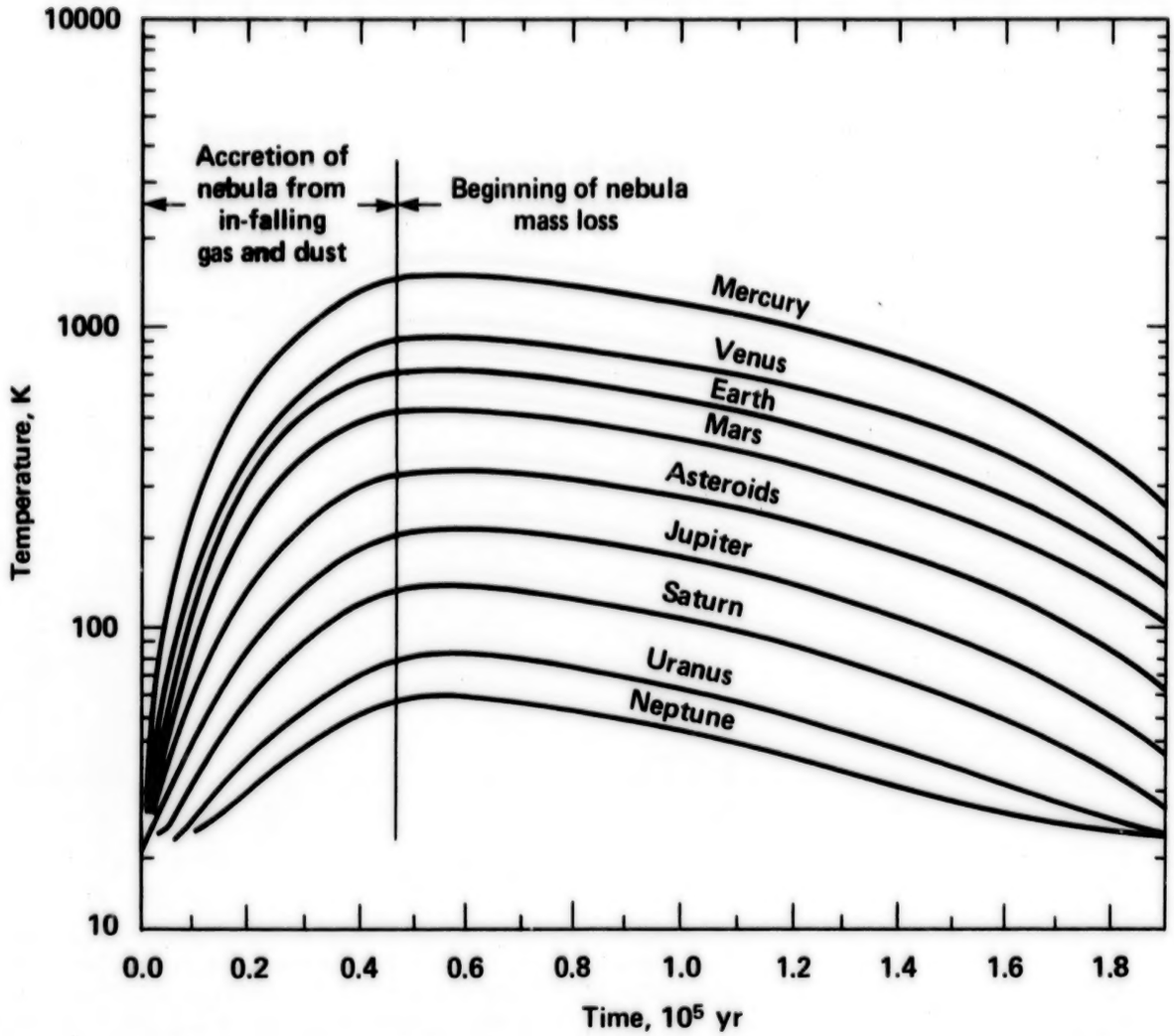

Figure 7.— Evolution of temperatures in one particular nebula model. Temperatures are shown at the positions in the nebula where the planets and asteroids are expected to form. From A. G. W. Cameron (1978), *Moon and Planets 18*, 5-40. ©1978 by D. Reidel Publishing Company.

in protostellar collapse in the form of interstellar dust and interstellar molecules accreted as mantles on dust (see chapter IV). This assumption seems reasonable in light of the low temperature (≤20 K) associated with Phase II of collapse (chapter V). In theory, some of the dust may already have aggregated to form objects as large as millimeters in size. Next we will examine the observational data obtained from studies of comets, meteorites, and interplanetary dust, and consider whether they may provide insights into the history of the biogenic elements and their compounds in the solar nebula. Along the way we will point out some outstanding problems. Finally, we will summarize some general lines of future research that may prove promising.

SOLAR NEBULA PROCESSES

Heating and Cooling

An important question is, to what extent were the interstellar dust and gas physically and chemically altered as they were accreted by the nebula? Depending on the distance from the protosun, their possible entrainment in convection currents, and the scale and dissipation times

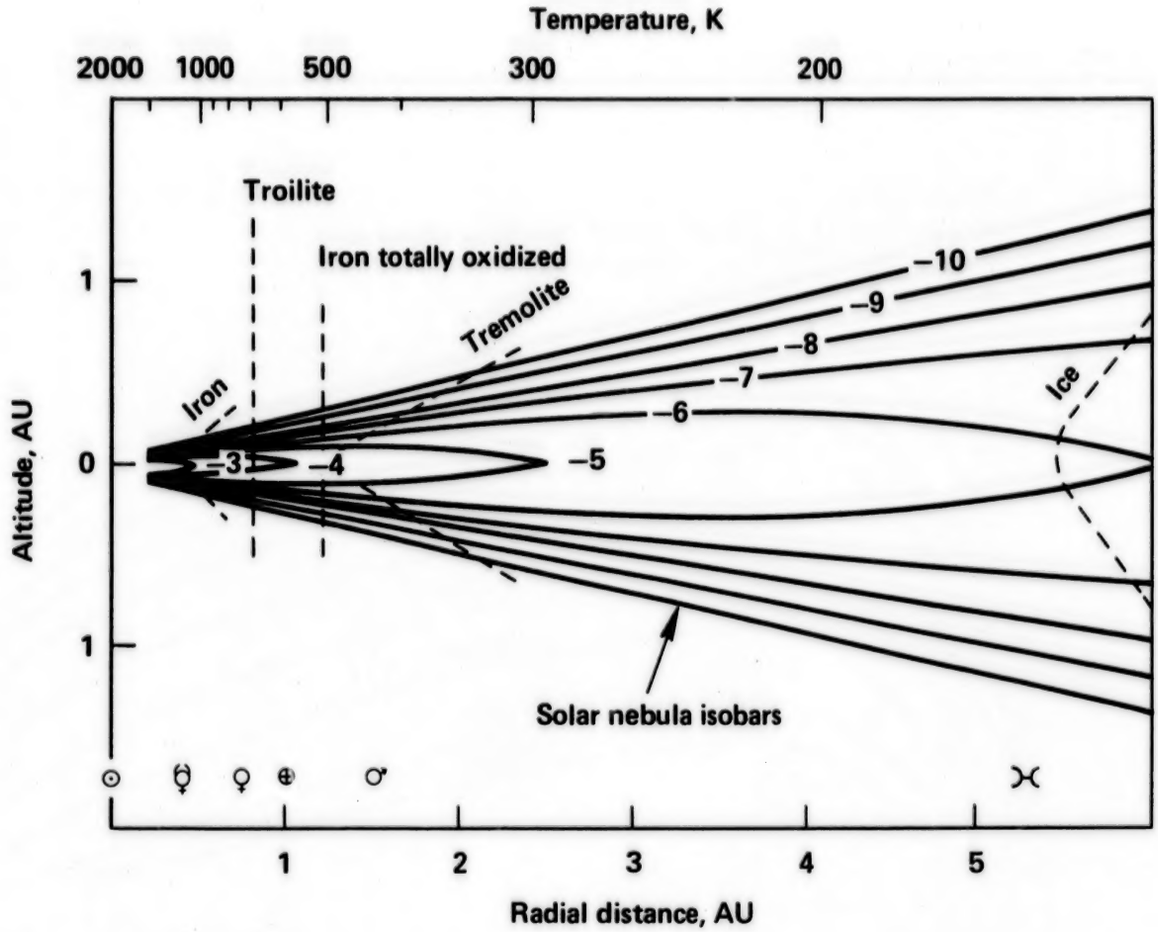

Figure 8.— Gas pressure (isobars; units are $\log_{10}$ pressure in bars) in the nebula model of figure 7 plotted as a function of radial distance from the protosun and altitude above the central plane during the warmest phase of evolution of the model. The respective positions in a chemical equilibrium model where several minerals would condense, or form by reaction, are shown with dashed lines. Reprinted with permission from *Planet. Space Sci.*, 30, R. G. Prinn, "Origin and Evolution of Planetary Atmospheres: An Introduction to the Problem," ©1982, Pergammon Press, Ltd.

of these instabilities, accreting dust grains may have evaporated only partially, or never at all. At the farthest reaches of the solar nebula, where temperatures may never have exceeded ~80 K, interstellar gas and dust could have accreted virtually unchanged into volatile-rich planetesimals, the protocomets. On the other hand, if interstellar grains had acquired mantles within which reactive chemical species (e.g., free radicals) were stabilized at very low cloud temperatures, even warming to ~40 K may have been sufficient to allow their exothermic recombination. Depending on the free radical abundances, the consequences may have ranged from a slight increase in grain temperature to ejection of condensates into the gas phase or disruption of the grain. Clearly clathrates of CH_4, CO, CO_2, and N_2, and ices of CO_2 and H_2O must have remained in cold nebular regions in order to survive. Progressively more refractory grain materials would have survived in increasingly warmer regions, but amorphous refractory grains could have been thermally annealed to more crystalline states. Similarly, gases accreting to the nebula, as they were warmed and compressed, may have chemically reequilibrated with each other and with dust only in part, or not at all.

Volatilizable organic matter that had accreted as mantles on interstellar grains would undergo varying degrees of evaporation or pyrolysis to yield both gases and more refractory residues.

As a result, transport of gas and dust from cool to warm regions of the nebula was likely to have caused changes in the elemental, isotopic, and molecular compositions of both the gas and solid phases. To balance the movement of material from cool to warm locations in the solar nebula, the reverse process would also have occurred. Cooling of hot gas and dust could have led to condensation of solid or liquid particles either directly from the gas, or onto unvaporized refractory seed crystals. Conversion of gaseous species such as CO, CO_2, NH_3, and H_2 to simple organic compounds and water could have occurred in the gas phase by a variety of processes, as well as on the surfaces of grains endowed with catalytic properties (see below). Further cooling would have permitted condensation and retention of these products on grains. Formation of grain aggregates eventually would have encapsulated them in their interiors. The net imprint left on the physical state and chemical and isotopic composition of materials that had been subjected to such a cyclical process is unknown, and merits consideration. The frequency with which gas, dust, and aggregates might have been cycled between warm and cool regions of the nebula is also unknown; however, multiple cycles do not seem implausible.

Complete evaporation and reequilibration of interstellar material would have been possible, to the extent that the material could have been transported from the cool outer to the warm inner nebula, close to the protosun, before it accumulated into objects that no longer advected with gas. Inferences from meteorites suggest that melting, partial evaporation, and reequilibration of some of the refractory mineral components probably occurred, and the likeliest region for this would have been in the inner solar system. However, the picture becomes less clear as we move out to larger radial distances, where the components of unequilibrated ordinary chondrites, carbonaceous chondrites, and comets are likely to have accreted into parent bodies. Recent isotopic, chemical, and petrographic analyses of meteorite (see below) provide little evidence to support chemical models of the nebula that assume complete evaporation or reequilibration of the grains and gas.

The onset of net cooling in nebular evolution would have allowed condensation and grain aggregation to supersede the evaporation of interstellar and nebula grains. In those regions of the solar nebula that suffered little or no warming up to this time, dust aggregation that had begun earlier would have continued until the nebula dissipated. One should keep in mind that as the nebula cooled it would become possible finally to condense, accrete, and preserve volatile and thermally labile substances in regions in which higher temperatures had prevented this earlier. Thus the biogenic elements and their compounds may have infiltrated the inner solar system late in nebular evolution, either by transport from greater radial distances or by accumulation of local material formed from cooling residual gas (or both). In any case, it is possible that substances accreted or produced in one part of the solar nebula were transported to and mixed with materials formed in other parts of the nebula. Consequently, the materials accreted into planetesimals may have had complex thermal histories and diverse spatial origins.

The Initiation of Condensation

The principal mechanism that initiates condensation may be viewed as a three-body reaction. If *A*, *B*, and *C* are gaseous atoms or molecules, and *AB** is a collision complex formed by *A* and *B*, then

$$A + B \rightleftharpoons AB^*$$

represents formation and dissociation of the complex; and

$$AB^* + C \rightleftharpoons AB + C$$

represents collisional deactivation. The two gas phase species, *A* and *B*, cannot simply stick together by themselves without disposal of their excess energy (kinetic energy, or the energy released by bond formation, or both). The overall reaction

$$A + B + C \rightarrow AB + C$$

converts smaller to larger species, and eventually to particles. In theory, complex formation and dissociation rates are strongly influenced by the size and bond energy of *AB**; the collisional deactivation rate is relatively insensitive to *AB** and *C*. Order-of-magnitude estimates based on

theory demonstrate that the slowest three-body processes are those involving atoms or small molecules. Thus the initial stages of molecular growth and aggregation that lead to dust formation are the slowest.

The rate at which a three-body association reaction proceeds also depends on the potential energy ("activation energy") barrier. At temperatures <500 K, the rates for most three-body processes are slow, as are the rates for most chemical reactions in the gas phase. These barriers are usually absent if *A* or *B* is an ion, if both *A* and *B* are free radicals, or if *AB* is not a molecular species but a weakly bound Van der Waals complex. Ion-molecule three-body association reactions are usually rapid at room temperature, and in the absence of activation energy, the rates of these reactions increase rapidly as temperature is decreased. Ions, therefore, can promote the condensation of gas to dust.

In general, it is likely that the nature of condensation products would have depended largely on factors governed by nonequilibrium kinetics rather than equilibrium thermodynamics. Among others, these factors include the chemical composition of the gas phase, the rates and temperature dependences of those physical-chemical transformations that yield polyatomic molecules or initial condensation clusters, the relative depletion of condensable molecules in high vs low vibrational states, and the degree of supersaturation attainable by condensable species in the gas phase. In the case of the biogenic elements and compounds, none of these factors is well understood, nor have they been considered carefully in the context of solar nebula models.

Despite the applicability of a general mechanism for condensation, the physical-chemical composition of the grains that may have nucleated from the biogenic elements and compounds in the solar nebula remains largely a matter of speculation. Condensable gases, including organic compounds, may have been inherited from the parent interstellar cloud, or they may have been synthesized in the solar nebula, or both. Grains may have arisen by the chemical synthesis of species with increasing molecular weight, by the physical aggregation of small molecules into clusters and complexes bound by Van der Waals forces, or by a combination of both processes. The ices of H_2O, CO_2, and NH_3, on the one hand, and clathrates of CO, CO_2, CH_4, and N_2, on the other hand, probably formed; but the composition of nebular condensates is difficult to predict, and probably was more complex than we have suggested.

Once condensation was initiated, the compounds in condensate particles would have remained in reactive contact with the nebular gases. To a greater or lesser extent, reaction with the gas phase would have brought the condensed compounds closer to the assemblage dictated by thermodynamic equilibrium than the initially nucleated species had been.

Thermodynamic Equilibrium as a Boundary Condition

A parcel of material in the nebula can be cooled either by moving outward, or by a decrease in temperature of the entire nebula. As this material parcel cools, three chemical time scales are of interest for determining the partitioning of volatiles between gas and condensate:

1. If the time scale for gas phase reactions is less than the cooling time scale, we can reasonably assume gas phase equilibrium.
2. If the time scale for gas to permeate into and react with condensed material is less than the cooling time scale, we have gas-condensate equilibrium.
3. Finally, if the time scale for migration and reaction of elements within the condensed material is less than the cooling time scale, we expect condensate equilibrium.

The opposite inequalities in these three cases imply the possibility for the appropriate disequilibrium cases. The three equilibrium cases are favored by high temperatures, slow radial mixing and nebula cooling, and in cases (2) and (3), by small grain sizes and slow accretion rates for these grains. In equilibrium case (3), and often in equilibrium case (2), the condensed material remains homogeneous over scales much larger than the sizes of individual crystals. Such cases are usually referred to as homogeneous accretion scenarios. The converse is heterogeneous accretion, which can result from either disequilibrium cases (2) or (3) and which would lead to distinct layering of condensed material.

The importance of these definitions is amply demonstrated by considering the manner in

which metallic iron, sulfur, and H_2O can be incorporated into condensed grains. Imagine the sequence of events in a material parcel which begins in figure 8 inside the orbit of Mercury and moves outward sufficiently slowly that equilibrium is always maintained. Metallic iron and calcium and magnesium silicate are expected to condense near 0.3 AU. As the parcel moves out, H_2S permeates the iron and converts some of it to troilite (FeS). At the same time, H_2O also permeates the condensate and oxidizes the remainder of the iron. At 1.2 AU no metallic iron remains, and further permeation of water causes hydration of the calcium and magnesium silicates to form hydrated silicates (tremolite, $Ca_2Mg_5Si_8O_{24}H_2$, has been used as an example in theoretical studies of condensation) at and beyond 1.3 AU. At this point all of the sulfur is condensed as troilite, and a few percent of the H_2O is incorporated in hydrated silicates. The remaining H_2O condenses as ice at 5.5 AU. (Needless to say, the process would also work in the reverse direction: condensed material that was moved from cool to warmer zones in the nebula would become dehydrated, and its iron would become reduced.)

Conversely, if the parcel moves outward so fast that equilibrium cannot be maintained, the iron remains as the metal, a few percent of the H_2S is condensed as Na_2S, and the remaining H_2S and all the H_2O do not condense until ice and solid H_2S form at and beyond 5.5 AU. A plethora of possibilities lies between these extremes. Some mineral associations in meteorites have been interpreted as reflecting condensation under quasi-equilibrium conditions in the warmer inner nebula. However, even in the gas phase there are important examples of disequilibrium, with major implications for the retention of carbon and nitrogen in condensed material. Therefore, evaluation of the kinetic barriers to attain thermochemical equilibrium for systems involving the biogenic elements and compounds is at least as important an endeavor as the determination of the boundary conditions imposed by equilibrium. Finally, it is possible that substances formed and accreted on grains as a result of equilibrium in one part of the nebula could have been transported to another region in which contributions would have been made by predominantly kinetically controlled processes. In this case the imprint of equilibrium might have become obscured.

Thermochemical Reactions

Thermochemical reactions can be divided conveniently into those in which the products and reactants are in thermodynamic equilibrium, and those in which the products and reactants must be related by kinetic considerations. If the innermost parts of the nebula were sufficiently hot, then the chemical time scale would have been less than the cooling time scale, and (as discussed in the previous subsection) equilibrium would have prevailed. For most thermochemical reactions of interest, the chemical time scale increases more rapidly with decreasing pressure and temperature than does the cooling time scale. Thus, as we move outward to cooler regions of the nebula we must reach a "quench surface" at which the chemical and cooling time scales are equal. Outside this surface the chemical time scale exceeds the cooling time scale, and the concentrations of species in this disequilibrium case must be determined in general by the solution of appropriate continuity equations. These equations include both chemical production and/or destruction reactions for each species and the convergence or divergence of the species' flux. It can be shown that if the e-folding distance[1] for the destruction rate of a species (the "chemical length") is less than the mixing length for turbulent mixing, then the mixing ratio of that species at the quench surface essentially determines its mixing ratio in all regions outside the surface. The position of the quench surface (i.e., the chemical time scale) and the value of the chemical length are functions of the activation energy of the reaction, among other variables, and will therefore vary with the nature of the chemical transformations being considered.

If the entire nebula were in equilibrium, then we would predict that the dominant carbon and nitrogen species at high temperature were, respectively, CO and N_2, while CH_4 and NH_3 would dominate at low temperatures. In a

[1] This term refers to the distance over which destruction of a species reduces its abundance by a factor of 1/e or the reciprocal of the base of the natural system of logarithms.

typical nebula model, the transition from a CO-rich to a CH_4-rich nebula occurs at the 10^{-4} bar, 680 K surface while the transition from N_2 to NH_3 occurs at the 10^{-5} bar, 330 K surface. In terms of the above discussion, this equilibrium is possible only if the quench surface for conversion of CO to CH_4 and N_2 to NH_3 lies well outside these latter transition surfaces. To determine whether this is indeed possible, we must examine the kinetics of these conversion reactions.

For conversions in the gas phase of a nominal nebula model, the quench surface for the conversion of CO to CH_4 lies at ~1000 K while the quench surface for the N_2 to NH_3 conversion occurs at ~2000 K. Thus if gas phase reactions were the only conversion paths available, we would predict that CO and N_2 would dominate throughout the nebula during its history, and that CH_4 and particularly NH_3 would be essentially absent.

However, the appropriate conversions can also occur in principle on the surfaces of grains in the nebula. For example, metallic iron grains are stable over the ~680–1350 K temperature range (being limited by evaporation at high temperatures and by oxidation to Fe^{2+} and reaction with H_2S at low temperatures). Metallic iron catalysts have been studied extensively in laboratories for their ability to promote reduction of N_2 to NH_3. If the available kinetic data for this conversion and a range of radial mixing times in a model solar nebula are taken into consideration, the overall rate of the reaction has been predicted to yield a maximum NH_3/N_2 ratio of 0.02. For this maximum an iron grain size of ~1 μm was assumed, which lowered the quench temperature to ~470 K; and catalyst poisoning due to sulfide formation was neglected. On the basis of these results, surface-catalyzed conversion of CO to CH_4 was also judged to be inefficient; and CO_2 was predicted to be more abundant than NH_3 throughout the solar nebula.

Admittedly, this type of calculation is strongly model-dependent in its assumptions about mass transport in the solar nebula, the chemical composition and size of catalytic grains, and the scaling of laboratory kinetic data to the nebular environment. Nonetheless, it yields testable first-order predictions about the compositions and abundances of some species containing the biogenic elements in a variety of solar system bodies. These provide a quantitative framework against which to compare predictions based on other processes.

A closely related transformation has been proposed to occur in the solar nebula. According to this so-called Fischer-Tropsch-Type (FTT) process, as the solar nebula cooled through the 600–350 K interval, adsorption of H_2, CO, and NH_3 on catalytically active magnetite, phyllosilicate, or other mineral grains led spontaneously to the synthesis of a variety of simple and complex organic compounds, CO_2, and H_2O. These products presumably were retained on the grains, and eventually accreted into planetesimals as the solar nebula cooled further.

Theoretical modeling of the FTT reactions appears to be extremely difficult because of the diversity of possible catalysts, the complexity and variability of the product mixtures, and the limited kinetic data available for such systems. Laboratory experiments have shown that the expected syntheses occur, but the conditions used departed strongly from those generally attributed to the solar nebula: for example, $H_2/CO \leqslant 100$ vs solar composition, total pressure ~1 bar vs 10^{-6} to 10^{-3} bar. Despite shortcomings in the simulation of nebula conditions, however, similarities were found when the molecular structures of many of the laboratory products were compared with those of the organic compounds extracted from carbonaceous chondrites. Moreover, the simulation experiments produced carbon isotopic fractionations between the resulting CO_2 and hydrocarbons that were similar in sign and magnitude to those found occurring between carbonate and soluble organic matter, on the one hand, and acid-insoluble organic residues in meteorites, on the other.

These similarities have been interpreted as evidence that the FTT reactions actually occurred in the nebula and were responsible for the carbon chemistry of these chondrites. Recently, however, new data on variations in the isotopic compositions of hydrogen, carbon, and nitrogen among phases in carbonaceous chondrites (see the next section of this chapter) raise doubts that the FTT reactions alone could explain the data. In fact, laboratory experiments have shown that the nitrogen isotope variations could not be explained by the FTT process. If only a few percent of the nitrogen in the nebula

were available as NH_3, strong demands would have been placed on the efficiency of the FTT reaction to produce organic nitrogen, demands which are not fulfilled in the laboratory experiments. Because the FTT synthesis model has assumed a prominent role in discussions of the chemistry of the biogenic elements in the solar nebula, a careful reassessment of the scope of its role is appropriate.

Photochemical Reactions

There are two potentially important sources of UV radiation available to drive photochemistry in the nebula. The first is enhanced UV emission by the young Sun. Enhancement by a factor of 10^4 over the Sun's present UV flux has been suggested from observations of young (T-Tauri) stars. If we assume an enhancement factor of 10^4 and a nebula lifetime of 10^6 yr, the potential number of molecular dissociations produced by this early enhanced UV flux would be equal to the number of molecules in a solar composition nebula of mass $\sim 10\ M_\odot$.

The second source is the UV radiation impinging on the nebular disk from surrounding stars. The typical UV flux at wavelengths <2000 Å in the interstellar medium is currently $\sim 10^8$ photons/cm^2-sec. If we assume a nebula lifetime of 10^6 yr and a radius of 100 AU, the potential number of molecular dissociations produced by UV starlight equals the number of molecules in a solar composition nebula of mass $\sim 10^{-4}$ solar masses. If these numbers are correct, they suggest that starlight is unimportant as a source of dissociating photons when compared to the young Sun, even if the latter's UV flux was merely comparable to that presently observed.

The existence of significant UV fluxes from the Sun during the time of existence of the nebula is a controversial matter, however. In addition, the photochemical zone driven by sunlight, which would comprise the inner nebula, will in general be at temperatures greater than those prevalent in the photochemical zone driven by starlight (which lies in the outer skin of the nebula). The degree to which the two zones are spatially distinct (and, therefore, at significantly different temperatures) will depend on the UV opacity of the nebula, which is a complicated function of the gas (e.g., H_2O, H_2); dust (e.g., iron, silicate, carbon); and ice densities. If the sunlight-pumped zone lies at temperatures ≥ 1000 K, then photochemically-produced nonequilibrium species will be rapidly destroyed by thermochemical reactions, and net yields of such species (e.g., simple and complex organic compounds) may be extremely low. The greatest potential for high yields of nonequilibrium species would exist in relatively cool regions of the nebula, which may be photochemically pumped largely by starlight. The role of photochemical reactions in the nebula needs to be carefully assessed, and this assessment should include considerations of the relative roles of sunlight and starlight, the influence of the evolving UV opacity of the nebula, and the contribution by turbulent mixing between warm and cool nebular regions to the overall yields of the photochemical products.

Lightning Discharges and Associated Thunder Shock Waves

The influence of lightning discharges and their associated thunder shock waves on the chemistry of the biogenic elements and compounds in the nebula has received relatively little attention. Charge separation induced by turbulent mass transport of gases and grains in the solar nebula cannot be excluded by any available evidence. On Earth, approximately 10^{-5} of the energy flux through the atmosphere is converted to lightning. Even if a minute fraction of the total gravitational energy dissipated in the solar nebula were converted to lightning discharges, an enormous amount of energy might have been available in highly concentrated local fluxes.

Direct observations of discharges in Jupiter's atmosphere indicate that they can occur in a solar-composition gas mixture containing liquid and solid condensates. Whether they can account for some of the CO, HCN, C2-hydrocarbons, and colored chromophores observed as nonequilibrium species in Jupiter's atmosphere, remains a controversial issue. In the solar nebula the dominant chemically active gases are expected to be H_2, CO, and N_2, whereas on Jupiter they are H_2, CH_4, NH_3, and H_2O. If water in liquid or solid particles or if a minimum pressure (or both) were required for discharges to take place, then they may have occurred in some parts of the nebula but not in

others. Theoretical bounds need to be placed on the amount of energy that might have gone into lightning discharges; and the chemical products of the discharges deserve elucidation, taking into account the probable temperature, pressure, and chemical composition of the nebular regions where such phenomena might have occurred.

Ionizing Radiation

The formation of organic molecules in dense interstellar clouds is attributed in large part to ion-molecule reactions initiated by cosmic rays. Penetration of ionizing radiation from external sources into the solar nebula would have been severely limited, except in its outer layer, by its high opacity. Evidence for the presence of the short-lived radionuclide ^{26}Al in the early solar system has emerged, however, from analyses of mineral inclusions in meteorites. These findings suggest that MeV positrons and gamma rays produced by ^{26}Al decay in solar nebula grains could have provided an internal source of ionizing radiation. A strongly model-dependent calculation has estimated that the resulting fractional ionization in the solar nebula could have amounted to 10^{-13}. Though not definitive, the calculation suggests a potential role for ion-molecule reactions. How important that role may have been merits careful assessment.

PRIMITIVE OBJECTS CONTAINING EVIDENCE OF SOLAR NEBULA PROCESSES

The history of the biogenic elements and compounds in the solar nebula may be revealed by studies of the natural materials that are most likely to have preserved a record of that period. If we use the degree of compositional similarity with solar elemental abundances as a criterion to select from among objects formed early in the solar system, it follows that the record has been preserved best in comets, and with decreasing degrees of integrity in carbonaceous chondrites and unequilibrated ordinary chondrites. Insofar as interplanetary dust collected in the stratosphere may be derived from comets, this constitutes a uniquely important sample of a type of material otherwise unavailable for direct study.

Comets

No direct information has ever been collected on the composition and internal structure of a cometary nucleus. Although it is clearly the source of all transient phenomena (the cometary coma, and tail or tails), the nuclear region is too tiny to be seen except as a pinpoint of light in the largest telescopes, and the nucleus itself is one or two orders of magnitude smaller. Our knowledge of the nature of cometary material is based entirely on circumstantial evidence, derived mainly from spectroscopic observations of those transient phenomena that result from the interaction of the cometary nucleus with solar radiation. As the nucleus approaches the Sun in its orbit through the solar system, solar heating apparently causes the sublimation of ices from its surface. The gases released form an exosphere (coma) that is continually lost to space. Solar UV radiation dissociates and ionizes its molecules and atoms on widely differing time scales. The chemical compositions of some of the molecular constituents are reshuffled and changed by fast ion-molecule reactions; the ions interact with the solar wind, and are blown away into the ion tail. This complicated chain of processes makes it difficult to reconstruct the nature of the unobserved "parent" molecules present in the nucleus from the observed "daughter" molecular fragments visible in the coma and the ion tail. Mineral dust is also released from the sublimating ices, and is blown away in the dust tail by solar radiation pressure.

The species that have been observed in cometary comas and tails are listed in table 5. A recent assessment of the elemental abundances inferred for the nucleus is summarized in table 6. Because large uncertainties are associated with these abundances, chemical models of the nucleus derived from them have qualitative rather than quantitative significance. Despite this shortcoming, the high abundances of volatile elements and the approximately solar relative abundances of the metals indicate that comets are very primitive materials preserved in the form of a conglomerate of dust and ices (or snows) of water and other volatile compounds.

The only available isotopic data on comets are rather imprecise determinations of $^{12}C/^{13}C$ from the isotopic splitting of the Swan bands of the C_2 molecule. These measurements yield a

TABLE 5.– OBSERVED SPECIES IN COMETARY SPECTRA

Organic[a]	Inorganic[b]	Metals[c]	Ions[d]	Dust[e]
C	H	Na	C^+	Silicates
C_2	NH	K	CO^+	
C_3	NH_2	Ca	CO_2^+	
CH	O	V	CH^+	
CN	OH	Mn	H_2O^+	
CO	H_2O	Fe	OH^+	
CS	S	Co	Ca^+	
HCN		Ni	N_2^+	
CH_3CN		Cu	CN^+	

[a,b]Seen in cometary heads as visual or UV emission lines or bands; except for HCN, CH_3CN, and H_2O, which are seen as pure rotation lines at radio frequencies. Signal-to-noise ratio poor for CH_3CN, very poor for H_2O.

[c]Seen as visual lines in semi-Sun-grazing comets only (except Na, which is seen in many comets, even outside 1 AU).

[d]Seen as visual or UV lines or bands at onset of plasma tails.

[e]Seen as IR emission bands at onset of dust tails.

TABLE 6.– RELATIVE ABUNDANCES (ATOM %) OF MAJOR ELEMENTS IN ICY PRIMORDIAL SYSTEMS

Element	Cosmos	Comets	Interstellar frost
H	2,660,000	2,400	3,300
C	1,200	370	1,200
N	200	150	370
O	1,800	2,200	2,100
S	50	55	90
Si	100	100	100

ratio of about 100 ±30, a value whose error bar embraces virtually all known solar system and terrestrial $^{12}C/^{13}C$ values. Despite reports of lower ratios (40 ±20) for some interstellar molecules, it is unclear whether the true interstellar ratio of $^{12}C/^{13}C$ in the vicinity of the solar system actually differs from the terrestrial value. Therefore, no definite answer can be drawn from the carbon isotopic data on the question of an interstellar vs a solar system origin for comets (see below). On the other hand, insight into this question may be provided by the isotopic composition of the other biogenic elements, H, N, and O; the patterns of isotopic fractionation exhibited by these elements among cometary molecules may ultimately reveal the nature of their production mechanisms and their source regions.

Two basic scenarios are commonly invoked to explain the origin of comets: (1) cold accretion of frosty interstellar grains during collapse of the protostellar cloud to form the solar nebula, or at a later time (by some unspecified mechanism); and (2) direct condensation from the cooling gas of the solar nebula. The first scenario implies that cometary chemistry can be deduced from the chemistry of dust and molecules in dense interstellar clouds, combined with models for the subsequent condensation of the molecules into icy mantles on the grains. According to this scenario, comets (or protocomets) may have

been vehicles by which the biogenic elements and their compounds in interstellar clouds were carried into and distributed among the solid bodies of the solar system.

The second scenario implies that comets are mixtures of materials produced by equilibrium and nonequilibrium processes that took place in an initially hot solar nebula, as it cooled. According to this scenario, comets represent ice-rich end-member planetesimals accreted late in the cooling history of the nebula in regions in which temperatures fell low enough to allow condensation of water ice and other volatile compounds. More data than are available on the molecular and isotopic compositions of species in the nuclei of comets will be needed to distinguish between these two origins.

Interplanetary Dust

Interplanetary dust collected in the stratosphere is composed partly of particles of meteoritic parentage ("chondritic"), and other unusual particles, possibly of cometary origin, referred to here as "primitive." Early reports describe these particles as aggregates of extremely small grains (0.1 to 0.5 μm) permeated with mostly amorphous (carbonaceous?) material of low atomic number. Their bulk major element compositions are approximately chondritic. The relatively volatile elements carbon, sulfur, and zinc occur in higher abundances than in ordinary chondrites, comparable to the levels in CI carbonaceous chondrites (see below) to within a factor of ~2.

On the other hand, several of the "primitive" particles have mineral contents, compositions, and morphologies quite unlike those in known meteorite classes. The interesting possibility has been raised that some of the primitive aggregates are presolar core-mantle interstellar grains whose carbonaceous mantles were modified during comet-forming processes. Whatever the origin of these aggregates, they appear to be sufficiently different morphologically from known materials to warrant detailed chemical and mineralogic investigations. Virtually no data are available regarding the biogenic elements and compounds in these aggregates, except for several semiquantitative measurements of carbon. These objects may provide the only real opportunities in the next decade to study cometary dust (albeit depleted of ices and other substances of comparable volatility).

Chondritic Meteorites

Chondritic meteorites are named after the spheroidal millimeter-sized objects called chondrules that occur abundantly in them. Chondrules appear to have solidified from the molten state while dispersed in a thin gaseous medium. According to current theories about their origin, chondritic meteorites (and the parent bodies in which they have resided for most of the age of the solar system) were formed in the solar nebula by accretion of components (grains and condensable gases) that experienced a variety of thermal histories. Among these meteorites, the carbonaceous chondrites (so called because of their carbon contents) are most similar to the solar atmosphere in their proportions of nonvolatile elements. They are, however, depleted in hydrogen, carbon, and nitrogen relative to the Sun by factors of about 0.0002, 0.05, and 0.02, respectively.

Carbonaceous chondrites consist of complex assemblages of chondrules, fine-grained minerals, and organic matter in various proportions. These assemblages are nonequilibrium mixtures, and they reflect wide variations both in environments of origin for the various components and in the chemical evolution of the parent bodies from which they were derived. We will include in our discussion carbonaceous chondrites of the CI, CM2, and CV3 groups. For present purposes the important differences between these groups lie in their content of volatile elements and minerals of high-temperature origin; the abundances of these are inversely correlated. Accordingly, the amount of carbonaceous matter (organic and inorganic) and hydrous mineral phases increases in the order CV3 < CM2 < CI, the carbonaceous matter from about 0.4% to 4% by weight. Inclusions containing minerals of high-temperature origin (e.g., melilite, spinel, and perovskite) occur most abundantly in CV3 meteorites, along with nickel-iron metal and the mafic silicates (olivine and pyroxene), which comprise the bulk of their mass. These minerals exist only in low to trace amounts in CM2 meteorites; and except for traces of mafic silicates, they appear to be absent in the CI meteorites.

Chondrules, mostly composed of olivine and orthopyroxene, occur most abundantly in CV3 type, less in the CM2, and not at all in the CI. Melilite, spinel, perovskite, and other high-temperature minerals that are predicted by thermodynamics to be the earliest condensates from a hot nebula gas of solar composition have been identified in small refractory-element inclusions in the Allende CV3 chondrite. Some workers have interpreted this to mean that quasi-equilibrium condensation occurred in the nebula, at least in regions of elevated temperatures, though other interpretations can also be drawn. Typically, the minerals and chondrules of high-temperature origin are embedded in an extremely fine-grained matrix containing virtually all of the chondrite's hydrogen, carbon, nitrogen, and sulfur.

Mixtures of phyllosilicates (hydrous mineral phases) comprise the dominant minerals (80 to 50%) in CI and CM2 meteorites, and a minor proportion of some CV3 meteorites. These hydrous minerals resemble some terrestrial clays, and the mixtures have bulk major element compositions similar to the pattern of solar abundances. This similarity has been interpreted as evidence of a primary origin for these substances in the solar nebula; but recent observations have shown that the phyllosilicates and the minor amounts of magnetite and carbonates that occur in examples of all three types of carbonaceous chondrites actually were formed as the products of low-temperature ($\leqslant$400 K) aqueous alteration of preexisting assemblages of anhydrous minerals in the regoliths of parent bodies. A similar explanation accounts for the sulfate found in CI and CM2 meteorites. On the basis of available data, nebular processes involving gas-dust equilibrium at low temperatures ($\leqslant$400 K) are not required to explain the mineralogy and petrology of carbonaceous chondrites. If such equilibration did occur, its manifestation in these objects appears to have been obliterated by the secondary alteration.

The organic matter in carbonaceous chondrites occurs in numerous forms (table 7). A complex, macromolecular material that is extremely fine in grain size ($\leqslant$500 Å) and virtually insoluble in solvents and most acids makes up the major carbonaceous component in all three types of meteorites. This incompletely characterized insoluble material appears to be composed of both amorphous and poorly crystallized components, the latter described as turbostratic carbon resembling highly disordered graphite. Although the sources and production mechanisms for this insoluble material are unknown, some subfractions of it serve as hosts for a variety of distinct noble gas components, including several with elemental and isotopic compositions that are difficult to explain in terms of solar nebula origins. The multiplicity of noble gas components implies multiple source regions, including extra-solar system ones for both the gases and the host materials. Moreover, these noble gas components are heterogeneously distributed among all the classes of carbonaceous chondrites, and the unequilibrated ordinary chondrites. Where the carbonaceous host phases acquired their noble gas contents and what the mechanisms were remain largely a mystery.

Solvent-extractable organic matter in the Murchison CM2 meteorite is distributed among a variety of compound classes (see table 7). These compounds comprise less than 30% of the total carbon and less than 0.05% of the total mass of the meteorite samples in which they were found. Some of these compounds have been sought and identified in other carbonaceous meteorites; but only Murchison has been studied in some detail, because of the availability of samples and their relative freedom from terrestrial contamination. Among the meteorites for which data are available, the extractable organic compounds appear to be heterogeneously distributed. For example, the total abundances of amino acids vary among CM2 meteorites, as do the relative abundances of individual amino acids. Differences of this sort are also observed between CI and CM2 meteorites. The reasons for these variations are unclear, but they may be related to differences either in the relative proportions of the compounds (or their precursors) accreted, or in the subsequent thermal histories of the parent bodies (or both).

The stereochemistry and molecular structures of the amino acids and carboxylic acids exclude a biological source (either terrestrial or extraterrestrial), and point to origins in abiotic processes. These conclusions also apply to other classes of compounds. The nature of the processes and where they occurred remain to be clearly established. Gas-solid reactions requiring

TABLE 7.– DISTRIBUTION OF CARBON IN THE MURCHISON CM2 METEORITE

Species	Abundance
Acid insoluble carbonaceous phase	1.3-1.8%
Carbonate and CO_2	0.1-0.5%
Hydrocarbons	
Aliphatic	12-35 ppm
Aromatic	15-28 ppm
Acids	
Monocarboxylic (C_2-C_8)	~170 ppm
Dicarboxylic (C_2-C_9)	+, not measured
Hydroxy (C_2-C_5)	~6 ppm
Amino Acids	10-20 ppm
Alcohols (C_1-C_4)	~6 ppm
Aldehydes (C_2-C_4)	~6 ppm
Ketones (C_3-C_5)	~10 ppm
Ureas	~20 ppm
Amines (C_1-C_4)	~2 ppm
N-heterocycles	
Pyridines and Quinolines	0.04-0.40 ppm
Purines	~1 ppm
Pyrimidines	~0.05 ppm
Poly-pyrroles	<<1 ppm
Sum:	1.43-2.35%
Total carbon:	2.0-2.5%

catalytic grain surfaces, electric discharges, and other gas phase reactions could have taken place both in the nebula and on parent bodies. Therefore, a variety of sources of the organic compounds is possible.

Recent isotopic studies of meteorite organic matter have revealed that large differences exist in the D/H, $^{13}C/^{12}C$, and $^{15}N/^{14}N$ ratios associated with different organic components in carbonaceous meteorites (table 8). Although the full implications of these findings remain to be revealed, it appears that the magnitudes of the isotopic variations and the differences in direction of the fractionations among components require more than one source region and/or more than one production mechanism to have been involved. If parent bodies contained protocometary material or interstellar matter that was relatively unaltered thermally in the nebula, then contributions from presolar system processes also need to be considered; these would include the ion-molecule and surface-mediated free radical recombination reactions thought to occur in the interstellar clouds (chapter IV) and the formation of carbonaceous grains in novae, supernovae, and cool evolved stars (chapter III).

Ordinary chondrites resemble CV3 chondrites in major element chemistry, but are more depleted in volatile metallic elements and the biogenic elements. The most primitive of these objects are the unequilibrated ordinary chondrites (UOCs). Their bulk carbon contents range up to about 0.5%, and some have been reported to contain hydrocarbons and possibly other extractable organic compounds amounting to several parts per million. Their fine-grained matrices, though showing signs of mild thermal metamorphism, are enriched in volatile substances relative to the chondrules and to matrices of other ordinary chondrites.

Local carbon contents in the UOC matrices exceed 40% in some cases, and graphite has been identified in them. Mostly bulk data are

TABLE 8.– RANGES OF ISOTOPIC COMPOSITIONS OF C, H, AND N IN THE PRINCIPAL ORGANIC FRACTIONS FROM CARBONACEOUS CHONDRITES STUDIED TO DATE[a]

Organic fraction	$\delta^{13}C$, %	δD, %	$\delta^{15}N$, %
Soluble organics from CI, CM2 chondrites	+5 to +40	+100 to +500	+50 to +100
Kerogens from CI, CM2, CV3 chondrites	-3 to -20	+600 to +1000	+10 to +30
Kerogen from Renazzo (CV2, anomalous)	-21	+2500	+150

[a]Delta values are defined in per mil units as follows, as for example in the case of carbon:

$$\delta^{13}C = \left[\frac{(^{13}C/^{12}C)_{sample}}{(^{13}C/^{12}C)_{standard}} - 1 \right] \times 1000$$

The standards used for C, H, and N, respectively, are Peedee Belemnite, mean ocean water, and air.

available for the isotopic compositions of hydrogen, carbon, and nitrogen; however, in some cases the D/H ratios in the water extracted by stepwise heating appears to be comparable to or higher than the highest values found in the acid residues of carbonaceous chondrites.

The relatively sparse data now available on the biogenic elements and their compounds in UOCs suggest some similarities with those in carbonaceous chondrites. The origins of these components in both types of chondrites are equally obscure.

UNSOLVED PROBLEMS AND RESEARCH OPPORTUNITIES

Throughout this chapter we have made reference to some of the outstanding problems that limit our knowledge of the history of the biogenic elements and their compounds in the solar nebula. These problems can be viewed in the context of two major questions: What were the physical-chemical processes operating in the nebula and earlier? What can the study of primitive objects reveal about the nature and occurrence of these processes?

Because large uncertainties exist in our understanding of the physical properties and thermal history of the nebula, a formulation of detailed answers to the first question would appear to be premature. Nonetheless, the solar nebula processes considered in the first section of this chapter, though perhaps an incomplete inventory, are manifestations of properties that commonly characterize solar nebula models and that are not in conflict with existing theory or observations. Their contributions to the chemistry of the nebula remain to be assessed in a general fashion, however. Model studies of the effects of these processes acting singly or in combination on the biogenic elements and compounds need to be carried out to define the conditions within which they would or would not have been significant. These studies may involve either laboratory or computer-based simulations, but in both approaches the range of conditions examined should include those consistent with existing physical models of the nebula. Most importantly, the elemental abundances of the reactants used should reflect the solar composition, although numerous options may exist in their molecular composition. If model solar nebula conditions turn out to be impractical to

simulate, then these studies should be conducted in a way that allows reasonable extrapolations to be made from the experiments to nebular conditions.

Simulations of solar nebula processes should be designed to afford quantitative data on the yields of products and their molecular and isotopic compositions. The former data can be translated into production rates and integrated into time-dependent models of chemical evolution in the nebula; the latter can provide patterns of molecular synthesis and isotopic fractionation among the biogenic elements that characterize the processes. These patterns can then serve as criteria for distinguishing the origins of the compounds of biogenic elements in primitive bodies of putative nebular origin.

Answers to the second question, concerning evidence of nebular processes preserved in primitive objects, require a more quantitative accounting of the biogenic elements and the compounds in them.

Remote measurements of the composition of comets can be made from Earth and spacecraft, but direct analysis of returned samples in terrestrial laboratories would be most desirable. Lacking spacecraft missions to comets, experimental, theoretical, and observational studies are needed that focus on the biogenic elements and compounds in efforts to reconstruct quantitatively the composition of cometary nuclei. The examination of interplanetary particles holds special importance, insofar as these may be derived from comets, and therefore they can provide ground truth for models of cometary composition and origin. Whether comets are composed of interstellar dust and gas or made up of solar nebula condensates (or both) is unknown, but supporting evidence for either case may be provided by determining the nature and extent of similarities in the organic matter of interstellar clouds, comets, and primitive chondrites.

More measurements are needed of the abundances and isotopic and molecular compositions of the biogenic elements and compounds in carbonaceous chondrites and unequilibrated ordinary chondrites. For example, although bulk isotopic data for hydrogen, carbon, and nitrogen are available for some meteorites, isotopic measurements of classes of compounds or individual compounds, though potentially of high diagnostic value, are rare. Molecular and isotopic measurements are most useful when they are integrated with mineralogical and petrographic observations. Together, these determinations provide a basis for distinguishing between primary effects attributable to the solar nebula and secondary effects arising from alteration in parent bodies. Comparison of the molecular compositions and isotopic fractionation patterns of the biogenic elements found in meteorites with those produced in synthesis experiments conducted under simulated nebula conditions should prove valuable in assessing the relative contributions of nebular processes. These comparisons may also shed light on the degree to which substances of interstellar origin survived processing in the nebula, and the extent to which mixing occurred in the nebula between spatially separated regions where different processes may have occurred. Pertinent to these considerations is the need to understand the origin of the relationship between the various noble gas components in meteorites and their carbonaceous host phases.

Naturally, models of the solar nebula and its thermal history will evolve as advances are made in the theory of protostellar collapse and in observations of star-forming regions of molecular clouds. The biogenic elements and compounds occur throughout the cosmos in a variety of chemical and physical forms which reflect the thermodynamic and kinetic processes that produced them. To the extent that comets, interplanetary dust, and primitive chondrites (and their asteroidal parent bodies) were formed in the solar nebula, increasing knowledge of the nature, abundance, and distribution of their contents of biogenic elements will also contribute to development of more constrained nebula models. More tightly constrained models, in turn, will lead to abandonment of obsolete ideas about the importance of some nebular processes and stimulate detailed examination of others for their power to rationalize and predict the abundances and compositions of the constituents of primitive bodies.

Additional Reading

Becker, R. H.; and Epstein, S.: Carbon, Hydrogen and Nitrogen Isotopes in Solvent-Extractable Organic Matter from Carbonaceous Chondrites. Geochim. Cosmochim. Acta, vol. 46, 1982, pp. 97–103.

Bunch, T. E.; and Chang, S.: Carbonaceous Chondrites – II. Carbonaceous Chondrite Phyllosilicates and Light Element Geochemistry as Indicators of Parent Body Processes and Surface Conditions. Geochim. Cosmochim. Acta, vol. 44, 1980, pp. 1543–1577.

Consolmagno, G. J.; and Jokipii, J. R.: ^{26}Al and the Partial Ionization of the Solar Nebula. Moon and Planets, vol. 19, 1978, pp. 253–259.

Delsemme, A. H.: Chemical Composition of Cometary Nuclei. Comets, L. L. Wilkening, ed., Univ. Arizona Press, 1982, pp. 85–130.

Fraundorf, P.; Brownlee, D. E.; and Walker, R. M.: Laboratory Studies of Interplanetary Dust. Comets, L. L. Wilkening, ed., Univ. Arizona Press, 1982, pp. 383–412.

Geiss, J.; and Reeves, H.: Deuterium in the Solar System. Astron. Astrophys., vol. 93, 1980, pp. 189–199.

Hayatsu, R.; and Anders, E.: Organic Compounds in Meteorites and Their Origins. Top. Curr. Chem., vol. 99, 1981, pp. 1–37.

Lewis, J. S.; and Prinn, R. G.: Kinetic Inhibition of CO and N_2 Reduction in the Solar Nebula. Astrophys. J., vol. 238, 1980, pp. 357–364.

Lewis, R. S.; and Anders, A.: Interstellar Matter in Meteorites. Scientific American, vol. 249, 1983, pp. 66–77.

McSween, H. Y.: Are Carbonaceous Chondrites Primitive or Processed? A Review. Rev. Geophys. Space Phys., vol. 17, 1979, pp. 1057–1078.

Morfill, G. E.: Some Cosmochemical Consequences of a Turbulent Protoplanetary Cloud. Icarus, vol. 53, 1983, pp. 41–54.

Ott, U.; Mack, R.; and Chang, S.: Noble-gas-rich Separates from the Allende Meteorite. Geochim. Cosmochim. Acta, vol. 45, 1981, pp. 1751–1788.

Wood, J. A.: The Solar System. Prentice-Hall, 1979, 196 pp.

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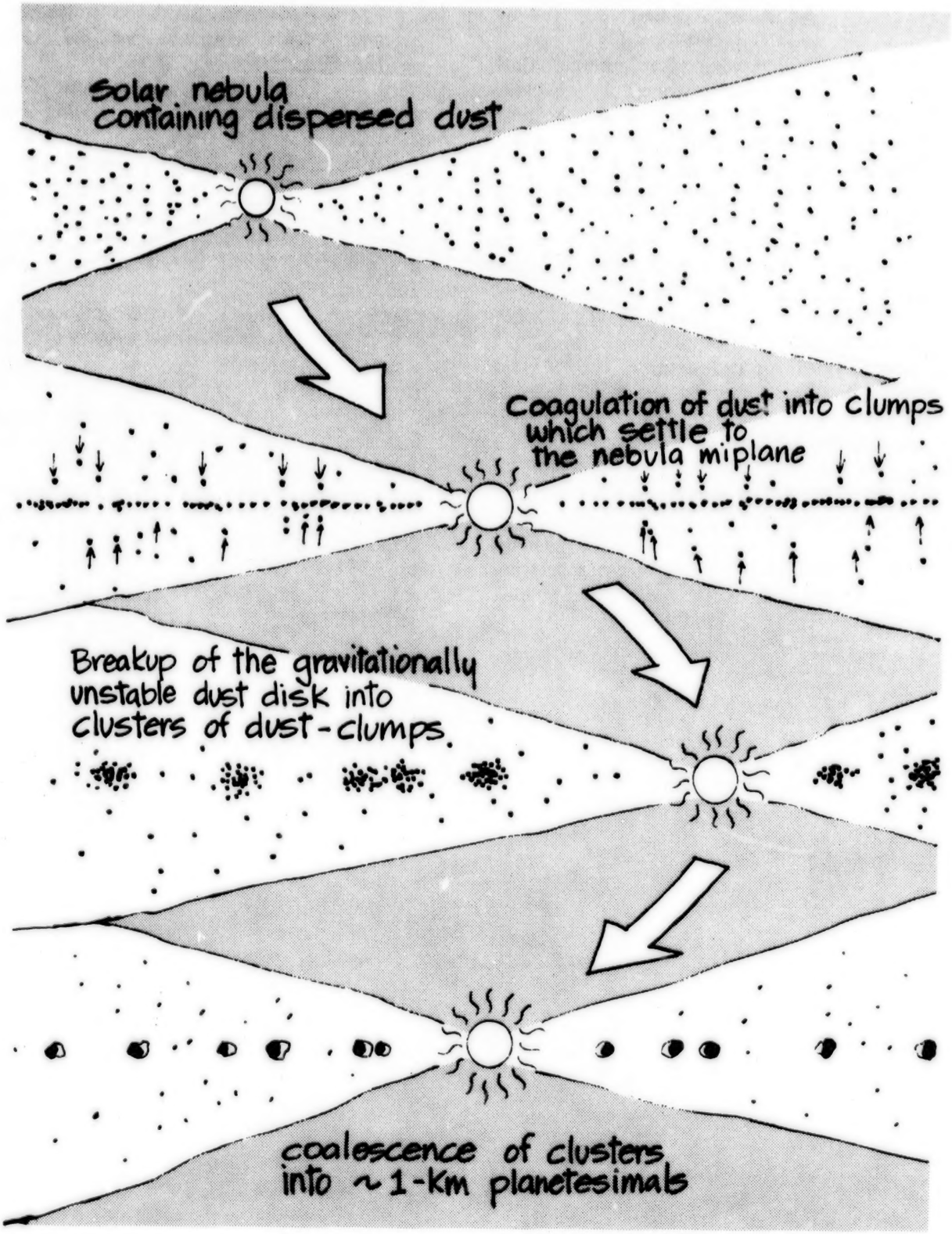

Figure 9.

VII

The Growth of Planetesimals From Dust

The previous chapter discussed the formation and early evolution of the solar nebula. In this chapter we will be concerned with the formation of planetesimals, by which we mean roughly kilometer-sized bodies, from the gas and dust present in the early solar nebula. The fate of these planetesimals, in particular their accretion into the next larger generation of bodies (which we will call "planetoids"), is the subject of chapter VIII.

This definition of a "planetesimal" may seem somewhat arbitrary, but it is based on the fact that the evolution of bodies smaller than about a kilometer in size is controlled by nongravitational forces. In contrast, the motions and interactions of bodies larger than about a kilometer in size are dominated by gravitational forces.

Very little is known observationally or experimentally concerning this stage in the formation of planetary bodies. Consequently, we shall concentrate primarily on theoretical evidence. In doing so it will be necessary to confine our discussion to a particular scenario, one in which the mass of the primitive solar nebula is relatively low. Alternative models that involve a so-called massive nebula invoke very different mechanisms for planet formation than those that are necessary in the context of low-mass nebular models. Planet formation in the former is typically thought to occur through the formation of giant gaseous protoplanets directly from the nebula by means of global gravitational instabilities (chapter VI). Such global instabilities are not possible in a low-mass nebula; planet formation must progress through the buildup of large bodies from smaller bodies. A schematic representation of the process and stages discussed in this chapter is given in figure 9.

The formation of a dust disk in the solar nebula is considered, and the evolution of such a disk as it pertains to the formation of planetesimals is discussed. Possible effects on the biogenic elements during disk formation and evolution are presented, and the chapter closes with a listing of some of the major unsolved problems concerning the formation of planetesimals and a listing of some near-term research opportunities.

THE FORMATION OF A DUST DISK

The starting point for the discussion to follow is sketched at the top of figure 9. It is assumed that dust is reasonably uniformly distributed throughout a gas-and-dust nebula. For the moment we will not be concerned with whether this dust is newly formed by condensation from the nebular gas, or whether it is dust that was present in the cloud that collapsed to form the solar nebula. The important point is that the dust is small (roughly a micron in size). In order to form a dust disk, these grains must settle to the equatorial plane of the nebula. As they do so, they will grow in size as they aggregate with other dust particles that settle at differing rates, and possibly also as vapor from the nebula condenses on them. This combination of settling and growth is a complex process, and attempts to determine quantitative details of it are very model-dependent.

Knowledge of the composition and physical state of the dust grains is critical to understanding their growth during the process of settling into the equatorial plane of the solar system. The sticking together of dust grains following a collision typically involves short-range forces such as van der Waals interactions, or perhaps electrostatic or ferromagnetic forces. Most studies to date indicate that van der Waals forces are the dominant ones to consider in the aggregation problem, except possibly in the case of metal grains.

Several studies have been conducted on the aggregation problem, and while results differ in detail, there is general agreement as to the time scale and the ultimate size that result from aggregation during settling. The quantity that is of most interest here is the expected size distribution of dust particles and aggregates that reach the equatorial plane. This is important for several reasons, one of the more important being the effect of the size of these solid bodies on the dynamical evolution of the dust disk.

The process of dust settling to form a disk within the gaseous nebula is complex, and a fully rigorous treatment of the problem has not been carried out. The major difficulty lies in the fact that as the dust grains settle toward the equatorial plane, they aggregate as noted above, but they also interact with the gas in the nebula. This latter interaction is affected not only by the chemical-physical character of the grain-gas exchange, but also by the dynamics of particles moving through the gas. Most calculations of this process use the so-called coagulation equation, which allows not only for the growth of particles due to collisions, but also the destruction or breakup of particles as a consequence of collisions that are too energetic. Studies of the combined settling and coagulation processes generally indicate that most of the mass in the dust disk is in the form of small dust grains (i.e., dimensions smaller than 10^{-3} cm), but that a significant number of grains are formed with sizes in the range 1-10 cm. The time scale for this settling process is relatively short, particularly in the inner regions of the solar nebula. Typical values for the time scale are of the order of 1000-2000 yr. One other important parameter is the thickness of the dust disk. Estimates vary, but most calculations yield thicknesses of a few kilometers in the inner solar nebula. This is to be compared to estimates of the thickness of the gaseous nebula in the inner solar system, viz., ~0.1 AU.

EVOLUTION OF THE DUST DISK

The evolution of the dust disk is depicted schematically in the lower part of figure 9. As might be expected, there is very little empirical information relating to this hypothetical phase in the development of the solar nebula. A wide variety of processes are operative in shaping the evolution of the disk. An example is the interaction between the gaseous nebula and the disk. Both the gas and the dust are undergoing rotational motion about the center of the nebula; however, the rotation rates of the two at a given distance from the rotation axis are not, in general, equal. This is because the solid particles, particularly the larger ones, move at Keplerian orbital speed, whereas the gas moves at slightly less than Keplerian orbital speed because of pressure gradients in the gas. The effects of this differential motion are discussed below.

It has been known for some time that the time scale for forming planetary-sized bodies through the process of accretion is very long, perhaps as long as 10^8 yr. This finding has led to a search for mechanisms that can assemble significant amounts of mass on a much shorter time scale. The mechanism that appears to have the most promise in this regard is that of a gravitational instability in the dust disk, analogous to the type of instability that would occur in a massive solar nebula. Whether such an instability can occur in the dust disk depends on whether the disk is relatively quiescent. If the overall disk is hot, or has some other form of internal energy that would promote turbulence in the gas, it is unlikely that gravitational instabilities could occur in the dust disk.

Detailed studies of the state of the dust disk indicate that if the particles in the disk are small (i.e., less than ~1 cm), the differential motion of the dust disk and the nebular gas will cause the dust disk to be turbulent, and therefore less susceptible to large-scale gravitational instabilities. On the other hand, if a

sufficient number of particles in the dust disk are larger than ~1 cm, it is unlikely that the energy input to the disk through the gas-dust shear motion will be sufficient to cause the disk to be turbulent. It is clear that we need to know the size distribution of particles in the dust disk to understand the dynamics of its evolution.

The nature of possible gravitational instabilities in thin disks has been studied by several authors and in several contexts (e.g., studies of galactic dynamics). In the case of the solar nebula, it has been shown independently by several authors that if the gravitational energy of the dust disk is large compared to its rotational energy, the disk can experience local gravitational instability. (This is often referred to as Goldreich-Ward instability, but the concept was discussed earlier by Safronov, among others.) If the disk is unstable, one can calculate the length scale of the instability from the surface density and rotational velocity of the dust disk. Using values for these parameters that are consistent with various models of the solar nebula, one finds that the wavelength of gravitational instabilities in the inner regions of the solar nebula would be $\sim 10^9$ cm.

A gravitational instability of this wavelength would be sufficient to encompass some 10^9 roughly meter-sized dust aggregations. These localized clusters of meter-sized bodies would be gravitationally bound units, each of which would collapse to form a single, roughly kilometer-sized body—a planetesimal. The time scale for the collapse of the swarm of objects is thought to be fairly short, ~100 yr or so. This type of instability would not be limited to one region of the nebula: similar instabilities and resultant clusters would be distributed throughout the dust disk. The interaction and subsequent evolution of these planetesimals is the subject of chapter VIII.

PROCESSING OF THE BIOGENIC ELEMENTS

The sequence of events and processes involved in the formation of planetesimals is complex and varied, and presents many opportunities for chemical and physical interactions that could affect the biogenic elements. A brief discussion of some of these interactions and their consequences is given here.

One of the more exciting findings from isotopic studies of a variety of elements in the meteorites, particularly neon and oxygen, is that there appears to be good evidence for extrasolar isotopic compositions. That is, the isotopic compositions in components of some meteorites differ from those that characterize the solar nebula as a whole; these components appear to have retained their characteristic presolar isotopic identities throughout the processing involved in the formation of the meteorites. The presolar compositions are most likely to have been preserved in small dust grains that were present in the cloud that collapsed to form the solar nebula. If some of these grains were never heated to high temperatures, their presolar compositions would have remained intact. Thus there is indirect evidence that the dust grains in the early solar nebula were, in part, surviving interstellar grains—not the products of condensation from a hot solar nebula. These grains would carry with them the biogenic elements in the forms that were established in interstellar space, or during very early phases in the formation of the solar system.

A crucial aspect of the processing of the biogenic elements during the formation of planetesimals is the structure and composition of the dust grains in the nebula. Structure is important for several reasons. If the grains were relatively hard spheres, the rate at which they could interact with the gaseous phase of the nebula would be much smaller than if the grains had a highly porous structure with a large surface-to-volume ratio. The rate of interaction is clearly important in determining whether chemical reactions can come to equilibrium, as well as whether and in what way surface saturation effects could become important in establishing the chemical compositions of the grains and the biogenic elements that are trapped in them. The structure of the grains is also important in determining the way in which grains grow through collisions with other grains; porous grains would have less strength than more compact grains, and would be more susceptible to fragmentation during collisions.

The process of planetesimal formation as described above contains several opportunities for fractionation of gas from dust, as well as

fractionation of one element from another. Severe gas-dust fractionation is likely to occur during the formation of the dust disk. At distances well above the equatorial plane of the nebula, the settling of dust will lead to an environment strongly enhanced in gas relative to other regions of the nebula. This same process will lead to a strong enrichment of dust relative to gas in the equatorial plane of the nebula. This type of gas/dust fractionation would probably have a major effect on the processing of the biogenic elements. In addition to the gas/dust fractionation, there is likely to be a significant fractionation among elements. The nature of this fractionation will depend on the structure of the grains, the temperature of the gas and the grains, and the process(es) that bind the various elements to the grains. For example, noble gases must be physically entrapped in the grain structures, whereas the biogenic elements can be bound to them by both physical and chemical means.

UNSOLVED PROBLEMS AND RESEARCH OPPORTUNITIES

Although there have been several studies of the phase of solar system evolution considered in this chapter, much remains to be done, particularly in the area of research that pertains to the processing of the biogenic elements. Among the major problems that remain to be addressed or solved, we identify the following: (1) specifying the thermal and chemical evolution of the dust; (2) identifying the principal carriers of biogenic elements in particular, and the volatile elements in general; and (3) describing the dynamical evolution of the dust disk in a less idealized theoretical framework.

Each of these problems involves several subproblems. For example, in order to make progress in determining the thermal and chemical states of the dust, we need a good model of the solar nebula. Such a model must contain information about the temperature and other state variables as a function of radial and vertical position, as well as information about the dynamics of the nebula. This is a very complex and interdependent problem, because the dust is the principal source of opacity in the nebula, and as such it controls the flow of radiation and thereby the temperature structure of the nebula. The temperature profile will also influence the dynamics of the nebula, particularly its tendency to become convectively unstable. Identifying the host grains for the biogenic elements entails the calculation of the chemical and physical evolution of dust grains under the conditions thought to typify a low-mass nebula. Of particular interest here is the formation/evolution of the carbonaceous material found in meteorites; this material appears to be the host phase for virtually all of the noble gases found in carbonaceous meteorites. Is this material formed entirely in the solar nebula, or was some significant fraction of the carbonaceous material brought to the solar system in the form of interstellar grains?

These and other related problems are very difficult to solve, but there are prospects for limited progress in several areas. Understanding the chemical and physical evolution of the dust should be a very high-priority area of near-term research because it has applications not only to this phase of solar system evolution, but to a variety of other phases as well. This research will involve theoretical and laboratory work, but efforts should also be made to study the structure and composition of interplanetary dust. These latter studies may provide valuable clues about the structure and composition of grains in space. The Space Shuttle and related zero-gravity facilities could provide excellent opportunities for the experimental study of grain growth in a space environment. It is especially important that laboratory studies be conducted in temperature and density regimes that accurately reflect those thought to occur in the solar nebula. Theoretical studies of the evolution of the nebula are also of high near-term priority, particularly those studies that shed light on the possible range of physical conditions in the nebula at this stage of its evolution. The models developed could then form the bases for more detailed studies involving fully time-dependent dynamical and chemical evolution of the gas-dust system.

Additional Reading

Hartmann, W. K.: The Planet-forming State: Toward a Modern Theory. Protostars and Planets: Studies of Star Formation and of the Origin of the Solar System. T. Gehrels, and M. S. Matthews, eds., Univ. Arizona Press, 1978, pp. 58-76.

Safronov, V. S.; and Ruzmaikina, T. V.: On the Angular Momentum Transfer and the Accumulation of Solid Bodies in the Solar Nebula. Protostars and Planets: Studies of Star Formation and of the Origin of the Solar System. T. Gehrels and M. S. Matthews, eds., Univ. Arizona Press, 1978, pp. 545–564.

Wetherill, G. W.: Accumulation of the Terrestrial Planets. Protostars and Planets: Studies of Star Formation and of the Origin of the Solar System. T. Gehrels and M. S. Matthews, eds., Univ. Arizona Press, 1978, pp. 565-598.

Wetherill, G. W.: Formation of the Terrestrial Planets. Ann. Rev. Astron. Astrophys., vol. 18, 1980, pp. 77-114.

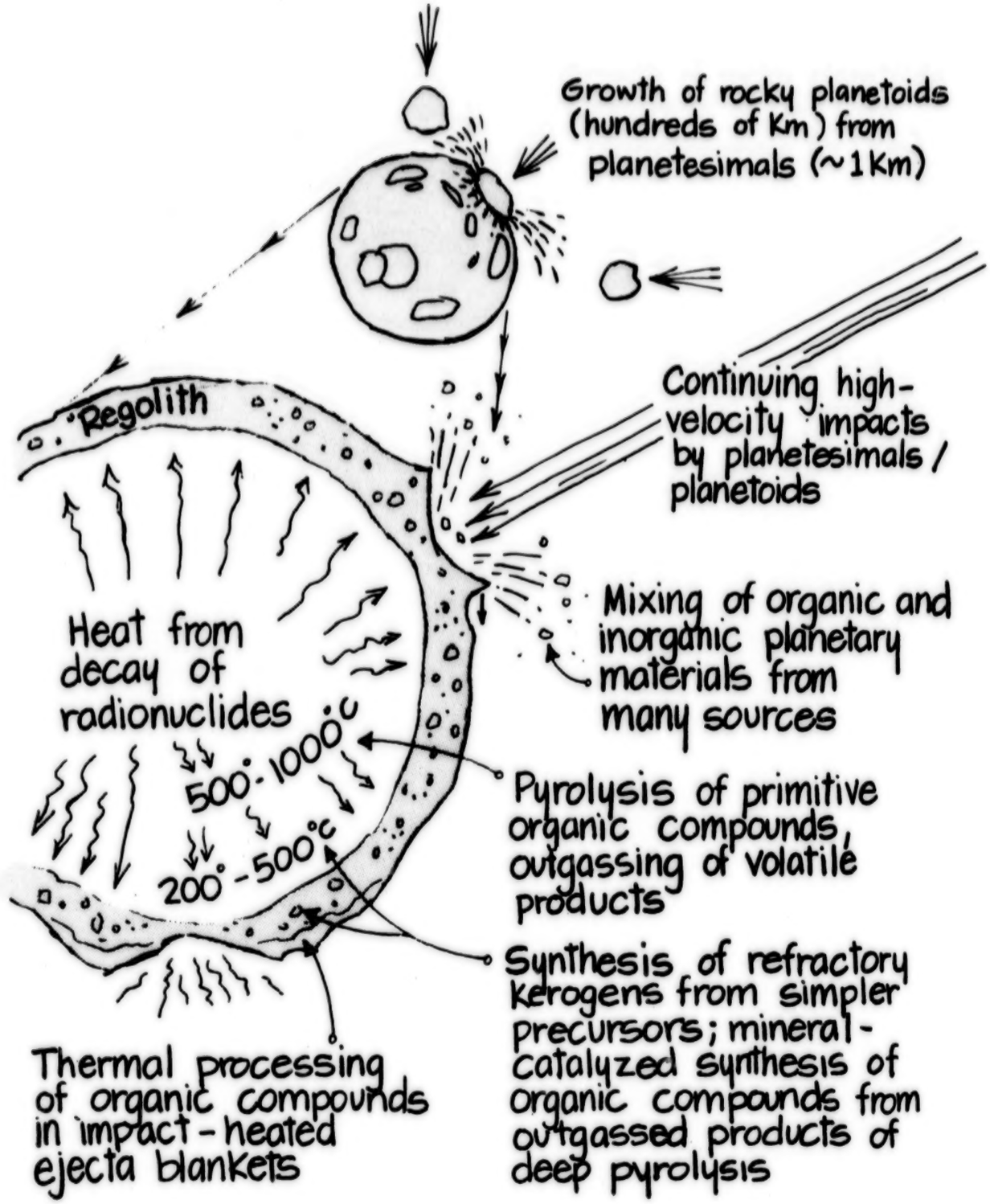
Growth of rocky planetoids (hundreds of Km) from planetesimals (~1Km)
Regolith
Continuing high-velocity impacts by planetesimals / planetoids
Mixing of organic and inorganic planetary materials from many sources
Heat from decay of radionuclides
500°-1000°C
200°-500°C
Pyrolysis of primitive organic compounds, outgassing of volatile products
Synthesis of refractory kerogens from simpler precursors; mineral-catalyzed synthesis of organic compounds from outgassed products of deep pyrolysis
Thermal processing of organic compounds in impact-heated ejecta blankets

Figure 10.

VIII

The Accumulation and Thermal Processing of Planetoids

In attempting to trace the biogenic elements from their formation to their incorporation in solid bodies of the solar system, we find that there were many opportunities for physical and chemical changes. In this chapter we are concerned with events and environments during the growth of planetoids from planetesimals, and also with changes that have occurred on and in these planetesimals in the eons since they accumulated.

We have divided the chapter into three parts. The first presents an overview of the changing environments of the biogenic elements, from small-body accretion through impact events on parent bodies, to regolith development, metamorphism, and differentiation (see fig. 10). The next section summarizes the observational data related to carbon-bearing small bodies (asteroids, meteorites, comets), and the effects that could have been caused by early environmental changes such as hydrolysis, degradation, and synthesis. Major outstanding questions and research opportunities are reviewed in the last section.

PLANETOID ENVIRONMENTS: THEORY

The dynamics of accretion of planetesimals (~1 km) into planetoids (tens or hundreds of kilometers) are complex. Here we will consider only in a qualitative way the possible effects of the process on biogenic elements and organic compounds. The accretionary growth of planetoids probably began by a rather gentle aggregation of many planetesimals and smaller bodies. The further growth of most of these planetoids into planets would have been strongly influenced by their orbital characteristics. If planetoid orbits were near-circular, collision velocities would be small and growth-favored, but in this case a growing planetoid would have only a narrow "feeding zone" to draw from, and the material it collected would presumably be homogeneous in character.

If planetoid orbits were more eccentric (and they are expected to become so after a few planets grow large enough to begin gravitationally deflecting the trajectories of objects that pass near them), larger collision velocities would result, and encounters would be destructive more often than constructive. However, this situation would lead to the mixing of planetary materials from a wide range of orbital distances and formation environments in the same planetoid.

A model by V. Safronov depicts a scenario wherein the earlier-formed Jovian planets perturbed icy planetesimals either inward toward the prototerrestrial planets for additional growth, or outward to become comets. In this way, planetary perturbations might account for the mixtures of low-temperature with high-temperature materials found in the more primitive meteorites, and for the mixture of ices and rocky material inferred for carbonaceous chondrite parent bodies and comets. Several lines of evidence indicate that the terrestrial planets accreted chiefly from relatively high-temperature, volatile-poor material, and that their inventory of volatile elements was probably supplied by a late-accreting "veneer" of volatile-rich planetesimals, possibly resembling certain carbonaceous chondrites, which must

have come from a different part of the solar system.

Temperature effects resulting from the gravitational energy of in-falling planetesimals would have been minor during the accretion of planetoids (i.e., asteroid-sized objects). The most important effect of the accretion of planetoids from planetesimals was the mixing of components from different source regions. Heating by the release of gravitational energy would, however, have been a significant factor in the thermal evolution of terrestrial planets. Heating by radioactive decay would have become important at several times during the growth and later history of planetoids and planets. If accretion occurred very rapidly, the decay of surviving short-lived ^{26}Al (half-life, 730,000 yr) may have been capable of melting planetesimals as small as a few kilometers in diameter. Slower accretion (i.e., a few million years to a few kilometers in diameter) would have limited the radioactive heat sources to ^{40}K and the actinides, which have much longer half-lives ($\sim 10^9$ yr) and thermal rise times. For most of the parent bodies of chondritic meteorites, which appear to have been ~100 km in dimension, maximum temperatures may not have exceeded 1000-1300 K. Metal alloys in the meteorites from these bodies retain a record of their subsequent slow cooling at rates of 1-100 K/10^6 yr.

Sustained temperatures of this magnitude would have destroyed early-formed organic compounds, but it is possible that internal heat generation would have had only indirect effects on the organic geochemistry of the near-surface zones of primitive planetoids and planets: (1) by supplying the relatively cool surface regions with volatiles expelled from the interior, presumably in the form of simple gases; and (2) by local surface heating as a result of volcanic eruptions. Some of the properties of meteorites may arise from the thermal processing of volatile elements in their parent planetoids. Among ordinary chondrites, for example, those of higher metamorphic grade (which presumably were sited deeper in the planetoid's hot interior) contain smaller concentrations of volatile elements than the chondrites of lower metamorphic grade (presumably representing cooler near-surface layers). This would seem to be the expected result of metamorphic outgassing; yet arguments have been raised, based on details of the volatile element abundance patterns, that these elements were not depleted by thermal outgassing from a planetoid, but had been depleted from the very outset in the nebular material which accreted to form that particular stratum in the planetoid. The mineralogic properties of meteorites strongly suggest that few, if any, meteorite parent bodies (or their precursors) escaped metamorphic heating, whatever the heat source may have been.

In addition to internal heating, other thermal episodes that could have affected volatile materials in the planetoids would have resulted from parent body surface events, mainly impacts with attendant regolith production and ejecta blanket development. Evidence of these violent events are clearly seen in the brecciated character of many meteorites, and are observed on planetary satellite surfaces. Impacts can generate enough heat to melt or volatilize rocky material.

As the images taken by a series of planetary spacecraft have shown, the surfaces of satellites have suffered severe bombardment. Most of the material near the surfaces of planetoids must have experienced some impact alteration, whether by melting, metamorphism, diffusive gas loss, fragmentation, or redistribution by ejection transport. Over time, numerous impacts produced regoliths that contain fragmented, melted, and shocked components of the parent body and, in lesser amounts, the impacting projectiles. Thus regoliths can contain an assortment of materials, which have experienced a wide range of thermal modifications. In addition, large impacts can generate thick ejecta blankets that could have preserved sufficient heat to weld ejecta components into coherent rocky material. Theoretical studies indicate that ejecta blankets ten to hundreds of meters thick were deposited on small bodies (<100 km). Depending on the grain size, degree of induration, blanket thickness, and impact flux, these deposits can have taken as long as centuries to cool.

That some planetoids actually melted and differentiated is evident from the igneous character of the achondritic meteorites. The surfaces of some asteroids (surviving planetoids) appear to have the same compositions as

certain of the igneous meteorite types, judging from the similarity of their reflection spectra in the visible and near-IR. Differentiated silicate meteorites are typically depleted in volatile elements; a few of them contain graphite, shock-formed diamonds, and sulfides. Lacking an atmosphere in which to recycle outgassed components and protect fragile organic molecules, differentiated planetoids are presumed to be inhospitable sites for prebiotic processes.

Events occurring subsequent to the formation of planetoids can have a significant effect on the chemistry of the biogenic elements they contain. The possibilities fall into three categories. First, preexisting organic compounds can be altered. Second, some new organic species may be synthesized from simple precursors. Third, organic materials from different sources may be mixed together, as in a regolith. All of these possibilities can conveniently be discussed in terms of parallels or contrasts with relatively well-studied terrestrial processes.

In carbonaceous meteorites of putative planetoid origin, organic matter is dispersed within a matrix of inorganic minerals. Terrestrial experience has shown that petrographic and mineral-chemistry studies of these inorganic components can set useful limits on the conditions under which they formed, and also on their post-accretional thermal histories. These limits, coupled with chemical, isotopic, and crystallographic characterizations of the organic components, provide the bases for judging whether the organic matter represents altered preexisting material, newly synthesized substances, a mixture of materials from different sources, or some combination of these possibilities.

The alteration of preexisting organic material can be compared to the formation and further development of "kerogen" in terrestrial sediments. In this process, simple organic molecules—initially soluble and, therefore, mobile—react to form a macromolecular product (kerogen) of such size that it is insoluble, and therefore immobile. This process of reaction and immobilization is not uniquely associated with biological materials; it will occur in any mixture of reactive organic compounds and is, in fact, the bane of the preparative organic chemist (e.g., "the attempted synthesis yielded tar instead of the sought-for product"). The formation of such a macromolecular product is inherently synthetic—a new product is formed—but it commonly involves some loss of material, and can be contrasted with the synthesis of new, mobile, small molecules from single-carbon precursors. It is an alteration process and, once it has occurred, the further development of the organic material is linked to that of the inorganic host, if any is present.

In terrestrial sediments, the postdepositional alteration of kerogen can be correlated in detail with a series of concomitant alterations of the inorganic sedimentary constituents. Time and temperature requirements are well established, and can provide a detailed background for the interpretation of analyses of extraterrestrial materials. The most informative analyses are extremely simple: elemental, IR spectroscopic, and X-ray diffraction analyses all provide usefully diagnostic indications of kerogen type and maturity.

The synthesis of new organic molecules from single-carbon precursors has no parallel in the postdepositional processing of terrestrial sedimentary organic matter. Nevertheless, it could accompany the formation of planetoids, or result from their later thermal evolution, with synthetic organic reactions being driven by energy from any of a number of different sources, both endogenic and exogenic.

Repeated cycles of accretion, breakup, and reaccretion could lead to the development of unusual mixtures of organic phases as materials with different developmental histories were combined. In terrestrial organic geochemistry, the coexistence of hydrogen-rich and hydrogen-poor organic material in the same rocks can be taken as evidence that either (1) the hydrogen-rich material migrated into the rock after metamorphism or (2) "premetamorphosed," graphitic organic material was somehow incorporated in the sediment during its formation. A choice between these alternatives, allowing a reconstruction of the sequence of events, can be made by studying the coexisting inorganic minerals. Similar temporal reconstructions should be possible after detailed and coordinated analyses are made of extraterrestrial organic materials and their inorganic hosts.

The isotopic composition of extraterrestrial organic material should record that of its elemental source, modified by (1) isotope effects associated with the initial synthesis of the organic material and (2) isotope effects associated with post-synthetic alteration processes like those described above. The recognition and measurement of such isotopic fractionations is difficult, and the precise and accurate reconstruction of initial isotopic distributions is, therefore, an extremely challenging task. To the extent, however, that any observed isotopic contrasts exceed those plausibly associated with fractionations due to reasonable synthetic or degradative processes, it may be possible to define organic materials that must have different sources (i.e., sources that escaped isotopic homogenization of the nebula).

Isotope exchange processes that occurred subsequent to synthesis are not expected to have had a major effect on organic carbon, hydrogen, or nitrogen. Even oxygen isotopic compositions should be relatively invulnerable to resetting by exchange, except in soluble materials that were actually dissolved in liquid water (in those same circumstances, the exchange of N- and O-bound hydrogen would also be expected, although that should not be of great importance in many cases).

PLANETOID ENVIRONMENTS: OBSERVATIONS

Investigations of meteorites, recovered interplanetary dust, and spectroscopy of asteroids and comets provide fragmental clues to the early formation and evolution of the solar system. Although we have many thousands of meteorite samples, our knowledge of meteorites is limited to a biased population, most of which has been collected over the last century. Spectroscopic observations of distant small bodies are of limited sensitivity and scope. Nevertheless, significant insights have been achieved and our knowledge will improve with more sophisticated efforts.

The following discussion will focus on observations related specifically to carbon-bearing hosts.

Carbonaceous Chondrites

These meteorites are least depleted in carbon, hhydrogen, nitrogen, and noble gases, and contain most of the elements in approximately solar proportions. Two major categories of carbonaceous material are observed. The larger comprises amorphous forms of elemental carbon together with macromolecular organic material that bears a marked resemblance to terrestrial kerogen. The smaller category consists of simple organic compounds that can be extracted by water and organic solvents. These latter organic compounds reportedly include many that are present in living systems: amino acids, hydroxy acids, polycarboxylic acids, purines, pyrimidines, fatty acids, sugars, and aliphatic and aromatic hydrocarbons (see table 7).

Until recently it was thought that these carbonaceous meteorites represented pristine material preserved from the time of its formation in the early solar nebula. However, recent findings strongly suggest that many components, and in some cases entire mineral assemblages, have been modified by heating events and aqueous alteration. Some carbonaceous chondrites have brecciated textures suggestive of final aggregation in a regolith environment. They contain inclusions that have experienced igneous temperatures, as well as organic molecules that could not have survived temperatures above ~500 K. Insoluble organic matter in these meteorites must have been introduced no later than the brecciation episode. For at least some carbonaceous chondrites brecciation was contemporary with the epoch of aqueous alteration, which appears from radiochronological evidence to have been one of the earliest recorded events in solar system history. Isotopic contrasts suggest strongly that soluble and insoluble organics are not genetically related, but the actual causes of the observed isotopic variability are unknown. The molecular composition of the soluble organic matter shows no unambiguous signature of possible alteration processes.

Unequilibrated Ordinary Chondrites

These meteorites contain numerous chondrules, much clastic material, and a complex

matrix of apparent relatively low-temperature origin. The biogenic elements are significantly depleted in them; the bulk carbon content is normally less than 0.5 wt %. The chemistry and isotopic compositions of carbon, hydrogen, and nitrogen in these meteorites are poorly understood. Bulk isotopic values are generally unexceptional, although a few meteorites have very large ratios of deuterium to hydrogen (D/H). Studies of the ultrafine matrix show an enrichment of carbon tenfold over the bulk content. Moreover, volatile and refractory elements as well as noble gases are enriched in this fraction; in some samples these exceed CI levels. Antimony, silver, zinc, and sodium are particularly enriched in these matrices, much as they are in the fine "fluffy" fraction of primitive interplanetary dust samples that is thought to have originated in comets. Although very little meteoritic material that has so far been investigated appears to be truly pristine, this volatile-element-enriched fraction would appear to be the least altered, and emphasis on a better understanding of its characteristics should be of high priority.

Differentiated Meteorites

Although differentiated bodies hold little hope for the retention of organic materials, studies of differentiated meteorites can add to our understanding of (1) the thermal processing of biogenic elements, and (2) the role that these elements play in the melting and generation of planetary basalts.

Differentiated meteorites consist chiefly of the basaltic achondrites (eucrites, howardites, diogenites); shergottites; nakhlites; and chassignites, all of which appear to define a coherent geochemical sequence. The sequence from the basaltic suite to chassignites is related in terms of an increase in alkali and volatile contents, and was probably established by low-pressure partial melting of several parent materials. The differentiated meteorites have formed in a manner analogous to terrestrial basalts and cumulates. Some of these samples have crystallization ages that are quite young (shergottites, 0.65×10^9 yr; and nakhlites, 1.3×10^9 yr) compared with other meteorites and lunar igneous rocks. In addition, Nakhla is a cumulate rock altered by hydrothermal fluids that were somewhat enriched in volatiles, including water and possibly CO_2. The important properties of this meteorite, from the perspective of biogenic elements, are the higher H_2O (and possibly CO_2) content, and the higher $f(O_2)$ of its magma, compared to those of the basaltic achondrite magmas. It has recently been argued that shergottites, nakhlites, and chassigny are derived from the surface of Mars.

The carbon contents of differentiated meteorites are in the range 500–5000 ppm, which is comparable to that for undifferentiated (unequilibrated ordinary) chondrites. Little is known about the isotopic composition of biogenic elements in the differentiated meteorites and their isotopic relationship to other meteorite types.

Asteroids

Although it seems likely that most, if not all, meteorites are derived from asteroids, and consequently the meteoritic abundances and chemical states of biogenic materials can be extrapolated to the asteroids, a rigorous connection has not been established. Thus we should not omit mention of the observations that have been made on asteroids directly. These consist of photometric properties (magnitudes, radiometric and polarimetric parameters, light curves, and especially spectral reflectance studies) that have been partially interpreted in terms of specific lithologies. The most significant findings from the point of view of biogenic elements appear to be (1) the prevalence among both the main belt and the Earth-crossing asteroids of objects whose spectra resemble the spectra of carbonaceous chondrites, (2) the spectroscopic evidence for clay minerals on some main belt asteroids (e.g., Ceres), and (3) the identification of some apparently differentiated asteroids, indicating that at least a few of these objects were internally heated to igneous temperatures. The extent to which the spectrally observed material on the surfaces of asteroids represents bulk underlying material is not known.

Comets

The gases that vaporize from cometary nuclei consist of molecules made up of hydrogen,

carbon, oxygen, nitrogen, and sulfur atoms (see table 5). Since the dust/gas mass ratio of the material coming out of the nucleus is in the range 0.5-1, the carbon, nitrogen, oxygen, and sulfur abundances in comets are much closer to the cosmic abundances than are those of carbonaceous chondrites. The great abundance of highly volatile compounds in cometary nuclei, and the source of comets from a vast swarm of nuclei (the Oort cloud) that orbit far outside the solar system, strongly indicate that cometary material is very primitive, having been preserved in its pristine state by the deep cold of space, and that comets are closely connected with the origin and early chemical evolution of the solar nebula. Uranus and Neptune, as well as the outer Galilean satellites of Jupiter and the icy satellites of Saturn, could have been made simply by the accumulation of cometary material.

Of all the smaller bodies in the solar system, comets seem to contain by far the largest amounts of the hydrogen-, carbon-, and nitrogen-bearing molecules that are needed to support biogenesis. Also, though it is poorly understood, there may be an important relationship between comets and interstellar frost (grains of condensed volatile molecules in dense interstellar clouds), since the atomic abundances of hydrogen, carbon, nitrogen, oxygen, and sulfur are very similar in the two cases. If a cold condensate of all known interstellar molecules were made into a big snowball and thrown into the solar system, not only would it develop a coma and an ion tail, but it would also show a spectrum virtually indistinguishable from that of a standard comet. Observations of comets reveal no evidence of thermal evolution that might have altered the primitive character of their constituents.

UNSOLVED PROBLEMS AND RESEARCH OPPORTUNITIES

Improved understanding of the effects of post-accretionary alteration requires (1) further definition of the nature of molecules accreted by planetesimals and planets, (2) a more precise understanding of conditions on freshly accreted planetary objects, (3) modeling and/or simulation of the fate of the biogenic elements and their molecules in primitive planetary environments, and (4) testing of possible scenarios using evidence from the terrestrial geochemical record.

More specifically, progress in topic (1) will involve further analysis of meteoritic organic matter, with the objective of answering the following questions:

1. Which mechanism(s) was/were responsible for the synthesis of the observed population of organic molecules in meteorites?
2. What relationship exists between the apparent thermal histories of organic and coexisting inorganic phases in meteorites?
3. Were these organic molecules synthesized in interstellar, nebular, or "planetoidal" environments?
4. How was preaccretionary organic matter distributed in the primordial solar nebula?

Progress in topic (2) will come from meteorite research aimed at elucidating the nature of parent body processes. Additional insight will be provided by comparative studies of crustal origin and early evolution on the Moon and terrestrial planets, on the one hand, and the satellite systems of Jupiter and Saturn, on the other. Specific questions that allow us to set bounds on the conditions on freshly accreted objects include:

1. What contributions to the thermal evolution of parent meteorite bodies were made by the several energy sources available: accretionary energy; endogenic energy (e.g., the decay of radioactive nuclides); and exogenic energy (e.g., solar radiation)?
2. To what temperatures and pressures were surface and near-surface environments raised, and for what lengths of time were they held there?
3. How, when, and from what sources were the volatile-rich materials bearing the biogenic elements and their compounds accreted to (and possibly redistributed among) solar system objects?

Topics (3) and (4) are intimately related, because little attention has been paid so far to the alteration of organic molecules in nonterrestrial environments. Current techniques, such as the use of isotopic fractionations to study kerogen maturation, could be usefully extended to these environments. Further meteorite study is also indicated to determine (for example) whether any of the molecular or isotopic

features of meteoritic organic matter are the result of alteration processes recorded in the inorganic fabric of the meteorites.

Significant progress can be expected to come from concentrated activity in the areas outlined above. However, it should be emphasized that still more profound insights would be expected if observations were extended to certain key environments currently either unexplored or observed with inadequate resolution. These include the surfaces of asteroids, comets, and the planet Mars. In that connection, it is important to note that the results of the Viking biology experiments, far from being "failures," actually led to the formulation of a most profound question: namely, why did life apparently *not* evolve in the environment of Mars? The answer to this question would lead to a fundamental improvement in our understanding of the origin and evolution of life on Earth.

Additional Reading

Bunch, T. E.; and Chang, S.: Carbonaceous Chondrites—II. Carbonaceous Chondrite Phyllosilicates and Light Element Geochemistry as Indicators of Parent Body Processes. Geochim. Cosmochim. Acta, vol. 44, 1980, pp. 1542-1577.

Chapman, C. R.: The Asteroids: Nature, Interrelations, Origins, and Evolution. Asteroids, T. Gehrels and M. S. Matthews, eds., Univ. Arizona Press, 1979, pp. 25-60.

Delsemme, A. H.: Chemical Composition of Cometary Nuclei. Comets, L. L. Wilkening, ed., Univ. Arizona Press, 1982, pp. 85-130.

Fraundorf, P.; Brownlee, D. E.; and Walker, R. M.: Laboratory Studies of Interplanetary Dust. Comets, L. L. Wilkening, ed., Univ. Arizona Press, 1982, pp. 383-412.

Greenberg, R.; Hartmann, W. K.; Chapman, C. R.; and Wacker, J. F.: The Accretion of Planets From Planetesimals. Protostars and Planets: Studies of Star Formation and of the Origin of the Solar System, T. Gehrels and M. S. Matthews, eds., Univ. Arizona Press, 1978, pp. 599-622.

IX

Directions for Future Research

In tracing the long path followed by the biogenic elements from their formation in stars and supernovae to their incorporation in the planets of the solar system, we have drawn attention to many places where the trail is dim and where additional research would greatly enhance our understanding of our biochemical heritage. Necessary research includes astronomical observations, a variety of types of laboratory studies, and theoretical analyses. In this chapter, we briefly review the most promising of these research opportunities. We believe the support of research in these areas would lead to important new insights into the cosmic history of the biogenic elements and compounds.

NUCLEOSYNTHESIS AND EJECTION TO THE INTERSTELLAR MEDIUM OF THE BIOGENIC ELEMENTS

Specific Sites of Nucleosynthesis

Astronomical observations should be made of specific sites where biogenic elements are being produced and ejected into the interstellar medium, with an emphasis on elemental and isotopic abundances in these regions. These observations will provide the basis for a clearer understanding of the enrichments of elements, isotopes, and dust grains in the interstellar medium attributable to specific classes of stellar objects, and will enable us to test models of stellar nucleosynthesis.

Observations of dust and molecules in circumstellar shells surrounding "late" stars are of great importance. Especially needed are high-resolution measurements at millimeter and IR wavelengths, and efforts to improve sensitivity in order to detect faint emission from the diffuse material in these extended regions. Similar studies in the visible wavelength range can probably be made with the space telescope. A large, deployable, orbiting reflector would greatly advance studies of circumstellar materials at submillimeter wavelengths.

Also badly needed are studies of elemental and isotopic abundances in the ejecta of novae and supernovae. In the case of novae, the need is for a capacity to direct observations quickly to a promising, but transient, event. Infrared observations would help identify novae in which there is prominent dust formation. Supernovae need to be studied at high spatial resolution: this is especially the case at visible wavelengths, where individual knots of the ejected material can be resolved and studied. The identification of dust containing carbon and other biogenic elements would be of great significance.

Observational Studies of Abundance Gradients in External Galaxies

In theory, the history of stellar processing and galactic evolution is recorded in the pattern of elemental and isotopic abundance variations in the galaxy. Observations of abundance gradients in external galaxies, when compared with those in our own, could reveal the extent to which cosmic evolution of the biogenic elements has taken similar or different paths in other regions of the universe.

High-resolution techniques (both spatial and wavelength resolution) at millimeter and IR

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wavelengths should be employed to measure the abundances of CNO isotopes in molecular clouds at various positions within nearby galaxies.

Elemental abundance gradients can be similarly resolved in these galaxies by making observations in the visible and UV regions of planetary nebulae and the HII regions they contain. The space telescope will increase the feasibility of such measurements.

Other Observational Studies in Our Galaxy

Cosmic ray experiments should be carried out using large detectors that have sufficient mass resolution to improve our knowledge of abundances of the heavy metal nuclides in the galactic cosmic rays.

Surveys in the IR should be made of a sufficiently large number of stars to allow an accurate estimate to be made of the rate at which the various nuclides are being added (ejected) to the interstellar medium.

CHEMICAL EVOLUTION IN THE INTERSTELLAR MEDIUM

Astronomical Observations

A careful inventory is required of variations in the nature and abundance of the biogenic elements and compounds in the interstellar medium. Such an inventory will serve as the foundation for an enlarged understanding of the sources, astrophysical processes, and physical-chemical mechanisms that govern the synthesis, transformations, and distributions of the biogenic compounds.

The continued identification by radio astronomy of complex molecules in space is of great importance. The inventory of molecules defines the complexity of the chemistry occurring in dense interstellar clouds. The recent tentative detection of interstellar glycine molecules underlines the relevancy of this work.

It would be most useful to identify transient, as well as more or less stable, molecules; transient molecules (free radicals and ions) are abundant in the interstellar medium. As quantum chemical predictions of the rotational frequencies of transient species improve, it should be possible to search directly for these species in space. (Studies of this type can also benefit laboratory chemistry, because transient species are normally seen only as laboratory intermediates, and their structures are poorly understood.)

Infrared studies need to be made of interstellar clouds and, as noted in the last section, circumstellar sources. Radio astronomy (at microwave and millimeter wavelengths) is the basic technique for studying dense clouds. However, the rotational spectra of molecules cannot easily be seen for those species that do not have dipole moments. Infrared spectroscopy can be undertaken for such species, which include important hydrocarbons such as methane and symmetric molecules such as hydrogen. Thus, IR astronomy serves as a valuable complement to radio astronomy. Circumstellar and protostellar sources with continuum IR backgrounds can be studied by IR absorption spectroscopy. These sources are themselves of extreme interest. Infrared studies can probe the broad resonances attributable to solid grains, in addition to gaseous molecular transitions. Better wavelength resolution for this technique will be crucial in establishing the spectral signatures of various mixtures and complex organic materials.

Experimental Studies

Research on the spectroscopy of molecules and grains composed of the biogenic elements is needed to expand the basis upon which chemical identifications of species in the interstellar medium can be made from astronomical observations.

Gas phase laboratory spectroscopy is the basis of all molecular astronomical studies. Of particular interest are studies of the rotational transitions of transient species and those stable species with incompletely studied spectra, especially in the high-frequency microwave (submillimeter) wavelength range.

The spectra of solid grains need to be investigated. Some laboratory simulations of the IR, visible, and UV spectra of grains have been carried out, but more work of this type is needed to decipher a variety of spectral features frequently seen by IR astronomers, in addition

to the classic diffuse bands that appear in the visible wavelength range.

Studies of ion-molecule reactions in the gas phase should also be carried out. The development of better models of the chemistry of interstellar clouds will require further laboratory studies of the rates and products of pertinent reactions. Some reactions are of particular importance; at the head of the list are radiative association processes that produce complex molecules. Almost as important is a knowledge of the branching ratios of neutral products arising from recombination reactions between polyatomic ions and electrons. Further investigation is needed of isotopic fractionations associated with ion-molecule reaction schemes, thought to have been responsible for some isotopic variations in primitive meteorites.

Experimental approaches need to be developed to study gas-grain interactions and the organic chemistry that could occur on or in various types of grains. Among the areas of interest are (1) the recombination or storage of free radicals; (2) the reactions promoted by photon or particle irradiation; and (3) the thermal or non-thermal mechanisms capable of ejecting molecules into the gas phase.

Theoretical Studies

Quantum chemical calculations are urgently needed in several areas of interstellar chemistry. Calculations of the rotational frequencies of transient species, which are difficult to produce in the laboratory, will aid astronomers in finding these elusive species in space and will also aid spectroscopists in finding them in the laboratory. Calculations on likely processes undergone by molecules adsorbed on grain surfaces should enlarge our understanding of grain chemistry and its role in the production of large molecules. Calculations of radiative decay rates of excited molecules are needed as input for radiative association calculations.

Theories of the rates of radiative association reactions need to be improved so the role of this process in producing molecules can be better assessed.

Models of dense interstellar clouds must be extended to include inhomogeneous physical conditions, radiative association processes, grain formation rates, and other complexities such as gas clumping. In addition, external chemical sources must be explored in more quantitative detail than has been done previously. This should include calculation of fractionation patterns in the different isotopic systems that would result from reaction schemes in molecular clouds.

PROTOSTELLAR COLLAPSE

Astronomical Observations

The biogenic compounds—e.g., CO, CS, H_2CO, HCN, etc.—should come into increasing use as molecular probes to elucidate the physical conditions, kinematics, and chemical fractionations that evolve during the stages of protostellar collapse.

Observational studies of small-scale structures in dark interstellar clouds are of great importance. Such observations are now becoming possible with the millimeter-wavelength interferometer telescopes at the California Institute of Technology, Pasadena, Calif., and at the University of California at Berkeley. In the future such studies could be greatly extended with instruments such as a millimeter-wave, very-large-array (VLA) radio telescope, or the orbiting large deployable reflector (LDR).

Observations need to be made of molecular and isotopic abundances in dense interstellar clouds and cloud fragments. These observations may be accomplished readily with sensitive single-dish millimeter-wavelength observations. A very modest investment in low-noise receiver technology will be required to reach the maximum potential.

Far-IR measurements from above the Earth's atmosphere will reveal conditions and processes in protostellar systems at stages of intermediate density and low temperature.

Near-IR observations of small-scale structures in dark interstellar clouds are of great importance in characterizing the inner zone of circumstellar nebulae.

Theoretical Studies

Several types of theoretical studies bear strongly on the evolution of the biogenic elements and compounds during protostellar

collapse. These address both the physical-dynamical and the chemical processes that come into play.

Multidimensional hydrodynamic calculations should be made of protostellar collapse dynamics, including the effects of rotation and magnetic fields. These calculations will permit assessment of the extent to which inhomogeneous distributions of the biogenic elements and compounds in interstellar clouds are preserved during collapse.

Calculations should be carried out to determine the chemical reactions and the isotopic fractionations that would arise from ion-molecule reactions in a collapsing protostar.

Calculations should be made to assess the effects of dust/gas interactions in a collapsing protostar on the chemical and isotopic fractionation of the biogenic elements between the gas phase and dust.

Laboratory Studies

Laboratory experiments should be designed to gain insight into the physical-chemical evolution of dust grains bearing the biogenic elements, under simulated interstellar and cloud-collapse conditions. These experiments will complement theoretical studies. Among the important issues are the extent to which chemical and isotopic fractionation occurs as a result of gas-grain interactions, and the efficiency with which trapping of volatile species occurs during grain growth.

CHEMICAL EVOLUTION IN THE SOLAR NEBULA

Laboratory Simulation Experiments

Hypothetical nebular phenomena can be simulated in the laboratory to provide a useful basis for assessing their contributions (if any) to the processing of biogenic elements and compounds during solar nebula evolution. Phenomena that merit study are listed below in order of decreasing priority, which corresponds inversely to the amount of study that already has been devoted to each process.

1. Gas-phase photochemistry driven by proto-solar radiation and starlight.
2. Pyrolysis or condensation of preexisting interstellar molecules.
3. Particle irradiation (ions, electrons) due to proto-solar wind, cosmic rays, and radioactive element decay.
4. Heterogeneous thermochemical reactions of the Fischer-Tropsch type.
5. Electrical discharges.

These simulation experiments should be conducted over the range of conditions (e.g., temperature, pressure, gas phase composition) indicated by existing models of nebular evolution, and they should yield data that can predict the products that would have been formed and possibly preserved in the primitive bodies of the solar system.

Laboratory simulations of nebular processes need to be carried out to determine the nature and abundances of organic compounds that would have been synthesized, and whether or not solid particles containing the biogenic elements would have been produced. The patterns of H,C,N,O-isotope fractionation among the reaction products, as a function of molecular structure, are expected to be characteristic of individual production mechanisms, and therefore of special importance for diagnostic purposes.

A basis for assessing the fate of carbonaceous grains during solar nebula evolution can be provided by measuring the rate of conversion of structurally amorphous grains (e.g., grains produced by the laboratory simulations proposed above, or from meteorite acid residues) to turbostratic and graphitic structures as a function of temperature; and also the rate of erosion of carbonaceous grains as a function of temperature, nebular gas composition, and fluxes of energetic particles or photons.

Grain-forming experiments in the presence of mixtures of noble gases should be carried out to determine whether the intimate association between trapped noble gases and carbonaceous grains in meteorites is the result of nebular processes. For comparison with meteorite data it would be essential to determine the distribution coefficients for the gases in the grains and the extent to which the gases were elementally and isotopically fractionated relative to the initial gas reservoir.

Sample Analyses

The organic matter in some primitive meteorites exists in many diverse molecular structures, and there are indications that extensive isotopic heterogeneity occurs among the various forms. To determine whether this structural and isotopic diversity is the result of nebular processing, however, requires that we obtain more systematic and quantitative information on the organic matter in primitive solar system objects.

In order to gain insight into the number and nature of production mechanisms involved in its synthesis, the organic matter in CI, CM2, CV3, and unequilibrated ordinary chondrite meteorites needs to be characterized with respect to (1) the H,C,N,O-isotopic compositions of the carbonaceous grains and of the extractable compounds as a function of compound class and molecular structure; and (2) the abundances and morphologies of carbonaceous grains with amorphous, turbostratic, and graphitic structures, and their distribution among meteorite types. Comparison of data from these studies with those obtained in the simulation experiments proposed above should elucidate the role played by nebular processes in the origins of meteoritic organic matter.

Some fundamental measurements of the biogenic elements in interplanetary dust particles need to be made in order to establish their degree of similarity to meteoritic materials and, by inference, to cometary dust. These measurements are listed below in order of practicality.

1. Morphological and crystallographic characteristics of carbonaceous grains within particles.
2. Bulk carbon abundances and isotopic compositions in individual particles or groups of petrographically distinct particles.
3. Bulk nitrogen abundances and isotopic compositions within groups of petrographically distinct particles.

For purposes of comparison with interstellar molecules, meteorite organic compounds, and the products of hypothetical nebular processes, identifications of parent compounds in the comae of comets should continue to be sought by Earth-based microwave observations and IR measurements made from Earth orbit.

Theoretical Studies

The energetics and kinetics of some hypothetical interactions among gas-phase and grain species should be modeled theoretically to assess the likelihood that they occur under plausible solar nebula conditions. Existing computational schemes and quantum and statistical mechanical methods can be brought to bear. Some of the interactions that merit study are:

1. Gas phase photochemistry driven by proto-solar radiation.
2. Thermochemical reactions in the gas phase involving interstellar molecules or fragments derivable from them by heating of hypothetical mantles of interstellar grains.
3. Growth of carbonaceous grains from free radical and ion-molecular species.
4. Reaction between gaseous water and anhydrous silicate grains to yield phyllosilicate grains.

THE GROWTH OF PLANETESIMALS FROM DUST

Theoretical Studies

Theoretical developments along several lines are required to elucidate the course of physical-chemical evolution taken by the biogenic elements and compounds as gas and dust in the solar nebula.

Detailed, self-consistent models are needed that describe the evolution of temperature and other state variables as a function of radial and vertical position in the nebula. These models will provide necessary bounds on the physical conditions which are applicable to experimental and theoretical simulations of nebular phenomena.

Calculations should be carried out, for likely nebular conditions, to determine how the rates of grain destruction and the rates of grain growth and coagulation vary from metallic to siliceous to carbonaceous to icy particles. The dependence of these rates on the porosities or hardness of these materials should also be assessed.

Calculations are needed to describe the chemical fractionation in the nebula that would

have resulted from settling of dust to the midplane.

The influence of carbonaceous grains or grains coated with carbonaceous matter on the opacity of the nebula should be assessed.

Laboratory Studies

A need exists for experimental approaches designed to determine the importance of grain structure and composition on the growth of dust into planetesimals. Laboratory studies should yield insights that are complementary to those provided by theoretical calculations.

Models for solar nebula grains need to be examined to determine the porosity or hardness that results from growth and coagulation in space. Relevant models would be (1) the inorganic and organic grains that make up interplanetary dust particles and (2) grains artificially synthesized under conditions simulating those in the solar nebula or interstellar clouds.

Collisions of grains under nebular conditions should be simulated to determine the relative "sticking efficiencies" of materials composed of the rock-forming elements, on the one hand, and the biogenic elements, on the other.

THE ACCUMULATION AND THERMAL PROCESSING OF PLANETOIDS

The study of meteorites and interplanetary dust particles must continue, with a goal of understanding the relationship between parent-body thermal histories and observed structural and isotopic characteristics of the biogenic compounds that exist in them. This aspect of sample studies complements the programs described in chapter VI, where the goal is to read a record of chemical processing in the nebula prior to the accumulation of planetesimals.

Laboratory Simulation Experiments

The alteration of preexisting organic matter and the synthesis of a new generation of compounds appears to have occurred in planetoids. To gain insight into the relationship between these processes and thermal histories, laboratory simulations should be carried out to ascertain the effects of endogenous and exogenous energy sources on the chemical evolution of the biogenic elements and compounds.

The phenomena that should be studied include the following:

1. Mild to strong metamorphism at depth within the body.
2. Pyrolysis and transport of volatiles from depth to the surface.
3. Outgassing of highly transient atmospheres.
4. Thermal and aqueous alterations during accretion and regolith formation.

The effects on the initial endowment of biogenic elements and compounds that need to be investigated are as follows:

1. Bulk elemental and isotopic fractionations.
2. Structural changes at the molecular and crystallographic level.
3. Synthesis of fresh organic matter with characteristic chemical and isotopic compositions.

Data from these experiments can be compared with the results of sample analyses.

Remote Observations of Small Bodies

Direct studies of the biogenic elements and compounds in comets, asteroids, and the satellites of the giant planets are needed to achieve two major objectives. The first is to substantiate the relationship between these bodies and the samples of meteorites and interplanetary dust now in hand. The second is to establish the present distribution of the biogenic elements and compounds in the solar system as a firm foundation upon which to build a better understanding of the way in which the dynamics of nebular evolution and planetary accretion distributed these elements and compounds throughout the solar system.

Determinations of the abundances of compounds and phases containing the biogenic elements can be made at several levels of increasing resolution and technological complexity:

1. Spectrophotometric observations from ground-based or Earth-orbiting astronomical observations.
2. Spacecraft missions with the instrumental capability for proximate or *in situ* measurements.
3. Detailed laboratory analyses of samples collected and returned to Earth by spacecraft.

END

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